

**Atmospheric Reactions of Polynuclear
Aromatic Hydrocarbons—Identification
and Quantitation of Oxygenated Species**

Report – Fiscal Year Apr.1/77–Mar.31/78

by

**Centre for Research on Environmental
Quality, York University**

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Atmospheric Reactions of Polynuclear Aromatic Hydrocarbons -
Identification and Quantitation of Oxygenated Species

Report for Fiscal Year April 1, 1977 - March 31, 1978

to

Air Resources Branch, Ontario Ministry of the Environment

for

OME Research Grant

Centre for Research on Environmental Quality
and Chemistry Department

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TABLE OF CONTENTS

<u>The Distribution of Polycyclic Aromatic Hydrocarbons (PAH) in the Air of Ontario Cities</u>		<u>Page</u>
1.	Introduction	1
2.	Collection and Extraction of Organic Matter	2
3.	Quantitative Distribution of PAH in Particulates of Four Ontario Cities	4
4.	Size Distribution of Particulates and PAH in Hamilton Air	13
	4.1 Particulate Collection	15
	4.2 Organic Fraction Extraction	17
5.	Results and Discussion	20
	5.1 Distribution of Particulate Matter and Dichloromethane Soluble Fraction at Hamilton Site 29025	20
	5.2 Particulate Size-Mass Distribution at Hamilton Site 29008	24
6.	PAH Distribution in Relation to Particle Size of Hamilton Samples	34
	References	39
 <u>The Photomodification of Polycyclic Aromatic Hydrocarbons (PAH) in the Solid State under Simulated Atmospheric Sunlight Conditions</u>		
1.	Introduction	41
2.	Experimental Methods	43
	2.1 Apparatus	43
3.	Sample Preparation and Reaction	47
4.	Results	51
	Rate of Decomposition and Half-lives of PAH (Tables 3 and 4)	63
	References	66

TABLE OF CONTENTS (continued)

	<u>Page</u>
<u>The Photodecomposition of Benzo(a)Pyrene (BaP) in Aqueous Media</u>	
1. Determination of Benzo(a)Pyrene Decomposition Rate	68
1.1 Preparation of Synthetic Solutions in Deionized Water	68
1.2. Preparation of Synthetic Solutions in Pond Water	69
1.3 Preparation of Fulvic Acids	69
1.4 Reaction System	70
1.5 Irradiation of BaP with Ultraviolet Light	72
1.6 . Extraction of BaP/Water Samples	74
1.7 Application of Gas Chromatograph and Fluorescence Spectrophotometer	74
2. Development of the Capillary Column	75
2.1 Type of Column Material and Method of Preparation	77
2.2 Etching Method	78
2.3 Deactivation of Columns	81
2.4 Coating the Columns	82
3. Capillary Chromatographic System	84
4. Preparation of Standard Solutions	85
4.1 Quinones	85
5. Photodecomposition of BaP	87
5.1 Photolysis of BaP in Deionized Water/Methanol	89
5.2 Photolysis of BaP in Pond Water	92
5.3 Identity of Photoproducts	98
5.4 Mechanism of BaP Photodecomposition in Deionized Water/Methanol	100
5.5 Mechanism of BaP Photodecomposition in Pond Water	105
References	108

The Distribution of Polycyclic Aromatic Hydrocarbons (PAH) in the Air of Ontario Cities

1. Introduction

The sources, reactivity, metabolism and carcinogenic properties of polynuclear aromatic hydrocarbons (PAH) have been reviewed in a 1972 monograph (1). These compounds occur in such diverse sources as fuel combustion products, motor vehicle exhaust, airborne particulate matter, cigarette smoke, sediments, high-boiling petroleum distillates, fumes from coke ovens, incineration of refuse and processed foods. Resultant mixtures of PAH from fuel combustion and other high temperature processings of organic materials are extremely complex. Organic fractions of airborne particulate matter have been found to contain over 100 different PAH compounds (2). Some of these PAH compounds have been shown to be potent carcinogens in biological assays but isomers of a specific aromatic group may differ greatly in their carcinogenicity. Thus, benzo(a)pyrene is a strong carcinogen, whereas the isomeric benzo(e)pyrene is non-carcinogenic, benzo(b) fluoranthene is carcinogenic but benzo(k)fluoranthene is not. Similarly, benzo(a)anthracene is positively carcinogenic whereas chrysene has been reported as negatively or weakly carcinogenic. Such isomers are very difficult to separate by gas chromatography, even on high-efficiency gas chromatographic columns.

Pierce and Katz (3) have found that approximately 70 to 90% of the total PAH content of airborne particulates are associated with particles in the respirable size range of less than 5.0 μm in diameter. Such respirable particles may exert a significant influence on the inhalation health hazards associated with toxic airborne substances. It has been estimated that about 60 percent or more of all human cancers are due to environmental agents (4). Consequently, it is important to develop effective, quantitative separation

techniques for the analysis of PAH compounds in air particulate samples, including the isolation of the individual components of isomeric groups that differ greatly in toxicity. Reported separation schemes employing thin-layer chromatography (5,6,7), adsorption chromatography and charge-transfer complexation (8), paper chromatography (9) and mass fragmentometry (10) have met with only limited or little success in the separation of isomers.

In this laboratory, procedures have been developed for the quantitative separation of PAH compounds from airborne particulate samples and for resolution of the individual members of each isomeric group by means of adsorption and partition thin-layer chromatography, followed by spectral analysis of individual compounds using fluorescence techniques (3,11,12,13). This report describes the results of application of these thin-layer chromatographic techniques, with certain improvements, for the fluorescence analysis and distribution of ten PAH compounds in samples of airborne particulates collected in four cities of Ontario.

2. Collection and Extraction of Organic Matter

Quarter sections of 100 fiber glass filters, containing suspended particulate matter collected by High Volume samplers at sampling sites in four cities of Ontario, were supplied by the Air Resources Branch of the Ontario Ministry of the Environment. The collection sites were as follows: (a) Toronto, Site 34007 - this location is influenced mainly by exhaust emissions from heavy motor vehicle traffic. (b) Toronto, Site 33003 - a suburban area that is subjected

to occasional motor vehicle traffic, especially by motorists proceeding to work in the early morning and returning in late afternoon. (c) Hamilton, Site 29025 - where the major source of particulates is derived from steel manufacturing and coke oven operations. (d) Sarnia, Site 14061 - where the major source represents oil refinery and petrochemical operations. (e) Sudbury, Site 77016 - the major source in this area consists of large nickel-copper smelting activities with emissions of particulates and large quantities of sulphur dioxide.

The particulate filters for each location were grouped into bundles representing seasonal, 3-month sampling periods over the 12-month period, April 1975 to March, 1976, as follows: April-June, July-September, October-December and January-March. Each filter bundle was installed in a glass extraction thimble, equipped with a sintered glass disc at one end and the unit was inserted in a soxhlet extraction apparatus. The filter bundles were extracted with 250 ml of pure dichloromethane for 8-12 hours.

After the extraction, the extraction thimble was allowed to cool to room temperature, then was rinsed with 25 ml CH_2Cl_2 and all washings collected in a receiving flask. The contents of each appropriate receiving flask were filtered through a clean, sintered glass filter funnel to remove any solid particles suspended in the solution. The receiving flask and sintered glass filter funnel were rinsed with 5-10 ml CH_2Cl_2 three times and the entire extract was then reduced to about 2 ml in a 50 ml pear-shaped flask by means of a Buchler flash evaporator in a water bath. The water bath temperature was maintained between 30°C and 35°C.

The remaining solvent was evaporated under a stream of dry nitrogen until approximately 1 ml of the extract remained. The residue was transferred

to a one-dram vial. The pear-shaped flask was rinsed 3 times with 1 ml portions of CH_2Cl_2 and the washings were also transferred to the vial. The solution was then evaporated to dryness under dry N_2 . The residue was weighed and stored in the dark at $0-3^\circ\text{C}$ in the refrigerator until thin-layer chromatographic resolution and spectral analysis could be performed. Details of this quantitative separation method have been described in the report to the Air Resources Branch for the fiscal year ending March 31, 1977 (14).

3. Quantitative Distribution of PAH in Particulates of Four Ontario Cities

The concentrations of the particulates and the dichloromethane-soluble extracts (DSF) containing the PAH fractions at the above sites are presented in Table 1. The higher mass concentrations of particulates and DSF ($\mu\text{g}/\text{m}^3$) were found at the Hamilton and Toronto sites. The lowest concentration of particulates occurred at Sudbury but the DSF concentration at Sudbury and Sarnia ($\mu\text{g}/\text{m}^3$) exhibited similar low levels.

Comparative concentration levels of ten PAH compounds for 3-month periods from April, 1975 to March, 1976 in the four cities are presented in Tables 2-6 in units of $\mu\text{g}/\text{g}$ of particulate matter (PM) and in nanograms (ng)/ 1000 m^3 of air sample. The total concentrations of the 10 PAH in the air of each city for the four seasons of the year are listed in Table 7. The relatively strong carcinogens, benzo(a)pyrene, benzo(b)fluoranthene and dibenzo(b,def)chrysene are of special concern as potential health hazards. Benzo(ghi)perylene is listed as non-carcinogenic (1), although this compound and benzo(rst)pentaphene have been found to be mutagenic in bacterial assay studies by Salamone, Heddle and Katz (15). The carcinogenic activity, if any, of naphtho(1,2,3,4-def)-

Table 1. Mass Concentrations of Airborne Particulates and Dichloromethane-Soluble Fractions (DSF) of Collections at Various Sampling Sites

Period	No. of Samples	Mean Mass Concentration $\mu\text{g}/\text{m}^3$	DSF Concentration $\mu\text{g}/\text{m}^3$	DSF/Particulate $\times 100$ percent
<u>Toronto Site 34007 (Bathurst St. at Highway 401)</u>				
April-June 1975	5	91.0	10.8	11.9
July-Sept. 1975	4	95.3	12.3	12.9
Oct.-Dec. 1975	6	82.8	12.8	15.4
Jan.-March 1976	5	77.8	8.4	10.8
<u>Toronto Site 33003 (Kennedy St. at Lawrence)</u>				
April-June 1975	6	76.6	6.8	8.9
July-Sept. 1975	5	63.5	6.0	9.4
Oct.-Dec. 1975	5	60.7	7.1	11.7
Jan.-March 1976	4	137.0	11.5	8.4
<u>Hamilton Site 29025 (Downtown)</u>				
April-June 1975	6	145.7	13.6	9.3
July-Sept. 1975	5	138.8	15.9	11.4
Oct.-Dec. 1975	5	69.4	10.6	15.3
Jan.-March 1976	4	83.6	7.5	9.0
<u>Sarnia Site 14061 (Near Mill Street refinery)</u>				
April-June 1975	4	61.8	3.0	4.8
July-Sept. 1975	5	46.5	3.6	7.7
Oct.-Dec. 1975	5	52.3	6.0	11.5
Jan.-March 1976	6	27.2	2.6	9.5
<u>Sudbury Site 77016 (Downtown)</u>				
April-June 1975	3	33.1	3.5	10.6
July-Sept. 1975	6	43.0	5.3	12.3
Oct.-Dec. 1975	5	22.3	2.9	13.0
Jan.-March 1976	6	23.4	3.6	15.4

Table 2. Comparative Seasonal Concentration Levels of PAH in Air of Ontario Cities
April 1975 - March 1976

Location: Toronto (Bathurst at 401)

Site Number: 34007

	Apr.-June 1975		July-Sept. 1975		Oct.-Dec. 1975		Jan.-Mar. 1976	
	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.
Benzo(a)pyrene	789	8.8	1047	11.0	1674	20.2	720	9.2
Benzo(e)pyrene	440	4.9	519	5.4	1294	15.6	781	10.0
Benzo(b)fluoranthene	866	9.7	798	8.4	1387	16.8	783	10.1
Benzo(k)fluoranthene	428	4.8	571	6.0	916	11.1	508	6.5
Perylene	102	1.1	123	1.3	193	2.3	108	1.4
Dibenz(def,mno)chrysene	46	0.5	44	0.5	234	2.8	34	0.4
Benzo(ghi)perylene	5849	65.3	7131	74.8	10,528	127.2	4413	56.7
Naptho(1,2,3,4,def)chrysene	270	3.0	362	3.8	538	6.5	228	2.9
Benzo(rst)pentaphene	58	0.7	60	0.6	150	1.8	67	0.9
Dibenzo(b,def)chrysene	313	3.6	183	1.9	446	5.4	213	2.7

Table 3. Comparative Seasonal Concentration Levels of PAH in Air of Ontario Cities
April 1975 - March 1976

Location: Toronto (Kennedy at Lawrence)

Site Number: 33003

	Apr.-June 1975		July-Sept. 1975		Oct.-Dec. 1975		Jan.-Mar. 1976	
	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.
Benzo(a)pyrene	657	8.7	408	6.2	729	11.7	814	5.9
Benzo(e)pyrene	478	6.3	375	5.7	400	6.6	791	5.8
Benzo(b)fluoranthene	890	11.8	693	10.6	1259	20.7	1829	13.4
Benzo(k)fluoranthene	328	4.3	285	4.4	597	9.8	519	3.8
Perylene	99	1.3	57	0.9	136	2.2	51	0.4
Dibenz(def,mno)chrysene	65	0.9	38	0.6	102	1.7	162	1.2
Benzo(ghi)perylene	5077	67.1	3303	50.5	4693	77.3	9814	71.6
Naptho(1,2,3,4,def)chrysene	410	5.4	201	3.1	300	4.9	2762	20.2
Benzo(rst)pentaphene	89	1.2	27	0.4	90	1.5	259	1.9
Dibenzo(b,def)chrysene	210	2.8	109	1.7	229	3.8	490	3.6

Table 4. Comparative Seasonal Concentration Levels of PAH in Air of Ontario Cities
April 1975 - March 1976

Location: Hamilton

Site Number: 29025

	Apr.-June 1975		July-Sept. 1975		Oct.-Dec. 1975		Jan.-Mar. 1976	
	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.
Benzo(a)pyrene	1404	9.6	2351	16.9	3498	50.6	1934	23.1
Benzo(e)pyrene	606	4.2	1407	10.1	3771	54.4	1607	19.2
Benzo(b)fluoranthene	813	5.6	2626	18.9	7841	113.1	2297	27.5
Benzo(k)fluoranthene	419	2.9	1425	10.3	5145	74.2	443	5.3
Perylene	141	1.0	283	2.0	403	5.8	347	4.2
Dibenz(def,mno)chrysene	70	0.5	128	0.9	369	5.3	150	1.8
Benzo(ghi)perylene	5809	39.9	7183	51.7	7532	108.7	6418	76.7
Naptho(1,2,3,4,def)chrysene	184	1.3	1017	7.3	2027	29.2	903	10.8
Benzo(rst)pentaphene	74	0.5	247	1.8	434	6.3	281	3.4
Dibenzo(b,def)chrysene	331	2.3	915	6.6	1132	16.3	704	8.4

Table 5. Comparative Seasonal Concentration Levels of PAH in Air of Ontario Cities
April 1975 - March 1976

Location: Southern Sarnia

Site Number: 14061

	Apr.-June 1975		July-Sept. 1975		Oct.-Dec. 1975		Jan.-Mar. 1976	
	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.
Benzo(a)pyrene	338	5.5	114	2.4	596	11.4	190	7.0
Benzo(e)pyrene	118	1.9	52	1.1	603	11.5	64	2.4
Benzo(b)fluoranthene	371	6.0	243	5.2	938	17.9	289	10.6
Benzo(k)fluoranthene	81	1.3	70	1.5	439	8.4	104	3.8
Perylene	27	0.4	13	0.3	87	1.7	19	0.7
Dibenz(def,mno)chrysene	23	0.4	8	0.2	44	0.8	7	0.3
Benzo(ghi)perylene	1038	16.8	1049	22.5	2700	51.7	1158	42.6
Naptho(1,2,3,4,def)chrysene	823	13.3	61	1.3	434	8.3	129	4.7
Benzo(rst)pentaphene	422	6.8	15	0.3	69	1.3	23	0.8
Dibenzo(b,def)chrysene	508	8.2	81	1.7	213	4.1	107	3.9

Table 6. Comparative Seasonal Concentration Levels of PAH in Air of Ontario Cities
April 1975 - March 1976

Location: Sudbury

Site Number: 77016

	Apr.-June 1975		July-Sept. 1975		Oct.-Dec. 1975		Jan.-Mar. 1976	
	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.	ng/1000 m ³ Air	µg/gm P.M.
Benzo(a)pyrene	175	5.4	111	2.6	342	15.3	444	19.0
Benzo(e)pyrene	23	0.7	45	1.1	255	11.4	317	13.6
Benzo(b)fluoranthene	255	7.8	173	4.1	417	18.7	650	27.8
Benzo(k)fluoranthene	57	1.7	74	1.8	197	8.8	271	11.6
Perylene	17	0.5	17	0.4	41	1.8	50	2.1
Dibenz(def,mno)chrysene	8	0.2	9	0.2	37	1.7	32	1.4
Benzo(ghi)perylene	779	23.9	1104	26.3	2321	104.0	3009	128.7
Naptho(1,2,3,4,def)chrysene	510	15.6	73	1.7	99	4.4	230	9.8
Benzo(rst)pentaphene	40	1.2	10	0.2	17	0.8	36	1.5
Dibenzo(b,def)chrysene	149	4.6	47	1.1	54	2.4	130	5.6

Table 7. Total Concentrations of 10 PAH in Air of Ontario Cities

April 1975 - March 1976

Season	Toronto Site 34007 ng/1000 m ³ µg/gm Air P.M.		Toronto Site 33003 ng/1000 m ³ µg/gm Air P.M.		Hamilton Site 29025 ng/1000 m ³ µg/gm Air P.M.		Sarnia Site 14061 ng/1000 m ³ µg/gm Air P.M.		Sudbury Site 77016 ng/1000 m ³ µg/gm Air P.M.	
April - June	9,161	102.4	8,303	109.8	9,851	67.8	3,749	60.6	2,013	61.6
July - Sept.	9,833	113.7	5,496	84.1	17,582	126.5	1,706	36.5	1,663	39.5
Oct. - Dec.	17,360	209.7	8,535	140.2	32,152	463.9	6,123	117.1	3,780	169.3
Jan. - March	7,855	100.8	17,491	127.8	15,084	180.4	2,090	76.8	5,169	221.1
Mean	11,053	131.6	9,956	115.5	18,667	209.6	3,417	72.7	3,156	122.9

chrysene is unknown. Of the remaining PAH listed in Table 2-6, benzo(e)-pyrene, benzo(k)fluoranthene, perylene and dibenzo(def,mno)chrysene (anthanthrene) are considered to have no carcinogenic potential.

The Hamilton site exhibited the highest concentration levels of PAH in units of $\text{ng}/1000 \text{ m}^3$ air, followed by the two Toronto sites. Comparative levels at Sarnia and Sudbury were much lower, with Sudbury exhibiting the lowest levels in three of the four seasons, on the basis of $\text{ng}/1000 \text{ m}^3$ air. At 3 of the 5 sites (Toronto, at Bathurst and #401, Hamilton and Sarnia), the highest total concentration levels occurred during the period October - December. On the other hand, at the Toronto suburban site (Kennedy at Lawrence) and at the Sudbury site, the highest total concentrations were found during the winter period, January - March.

The mutagen, benzo(ghi)perylene, occurred in relatively high concentrations at all of the sampling sites. Since the only common, large scale activity that could result in similar emissions at all sites in these four cities is the exhaust gases from motor vehicle traffic, it is probable that this PAH is one of the principal products in the organic polycyclic fraction of the particulates discharged from motor vehicles.

It is presumed that the surprisingly low levels of particulate matter and PAH in Sudbury air, notwithstanding the vary large scale of nickel-copper smelting activity about 5 miles distant, are due to the high efficiency performance of the electrostatic precipitators and the remarkable degree of dispersion of emissions from the 1250 ft. high smelter stack.

Published data containing concentration levels of some of these PAH compounds in the air of New York City (16), average of several U.S. cities (17), and in Antwerp (18), Ghent and Milan (10), are presented in Table 8. The Hamilton air levels of benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(ghi)perylene are considerably higher than the corresponding New York City concentrations.

4. Size Distribution of Particulates and PAH in Hamilton Air

Hamilton, Ontario is a heavily industrialized city with a population of 312,000, situated at the western end of Lake Ontario. It is of considerable interest in pollution studies because of the influence of a well developed lake breeze in the summer, as well as the presence of an escarpment to the south of the central city rising to 300 ft. above the city and oriented almost parallel to the direction of the lake shore. As a result of the concern of the community with air pollution, several studies have been undertaken (19,20,21). The study reported in Section 3 on the distribution of polycyclic aromatic hydrocarbons in the air of four Ontario cities had revealed that a significantly high content of carcinogenic PAHs exists in the atmosphere of Hamilton, Ontario (22). Such high concentrations of the various carcinogenic PAHs may indicate a potential health problem to some residents in Hamilton. For this reason, a more thorough investigation of this pollution problem in Hamilton was undertaken in order to provide information for the implementation of appropriate control measures.

Table 8. Comparative Concentration Levels of PAH in U.S. and Other Cities

PAH Compound	New York City (16) ng/1000 m ³ Air	Average U.S. Urban (17) ng/1000 m ³ Air	Antwerp (18) µg/g Part.	Ghent (10) ng/1000 m ³ Air	µg/g Part.	Milan (10) µg/g Part.
Benzo(a)pyrene	1150 - 1300	5700	((51	5200	60	46
Benzo(e)pyrene	1400	5000	(
Benzo(b)fluoranthene	800	2300-7400 (Detroit)	((83	7700	90	68
Benzo(k)fluoranthene	600	500-2000	(
Perylene	100-200	700	5	-	-	-
Benzo(ghi)perylene ^a	900	8000	12	-	-	-
Dibenzanthracenes	-	-	3	-	-	-

^a Antwerp concentration includes anthanthrene

The size and composition of suspended particulate matter is of primary concern when attempting to assess inhalation health hazards of an exposed population. It is now generally accepted that the degree of respiratory penetration is a direct function of the diameter of a particle suspended as an aerosol (23,24). Recent studies have also shown that a number of potentially toxic and carcinogenic trace constituents predominate in small, lung-depositing particles of urban aerosols (11,25) and in the smallest particles emitted from high-temperature emission sources (26,27). Thus a study of the size distribution of the suspended particulate matter, the monthly distribution of PAHs, and also the distribution of various PAHs according to particle size would be useful by providing more thorough information on this pollution problem in the Hamilton area.

4.1 Particulate Collection

Samples of suspended particulate matter were collected at the Hamilton Barton-Wentworth Station (Site 20925) using a standard High Volume Sampler. Suspended particulates were collected at a volume flow rate of 40 to 60 cu. ft./min. (1.13 to $1.70 \text{ m}^3/\text{min}$) for periods of 24 hours.

Aerosol samples were collected by five-stage Anderson Hi-Vol cascade impactors at Hamilton, West Central Region, North Park Station (Site 29008). When operated at a flow rate of 20 cfm (566 liters/min), the sampler fractionates suspended particulate matter into five aerodynamic size ranges according to the calculated 50% cut-off diameters given in Table 9.

Prior to particulate collection, the impactors were carefully assembled with fiber glass collection media of pH 6.5 and installed on the

Table 9. Aerodynamic size range of suspended particulate matter collected with Anderson Hi-Vol cascade impactor

Stage no.	Size range (μm)
1	≥ 7.0
2	3.3 - 7.0
3	2.0 - 3.3
4	1.1 - 2.0
5 ^a	≤ 1.1

^aStage 5 is the backup filter (20.3 x 25.4 cm glass fiber)

Hi-Vol sampler. Before and after each sampling period of 24 hrs., the filters were conditioned at a constant relative humidity ($50 \pm 2\%$) and temperature ($22^{\circ} \pm 2^{\circ}\text{C}$) for 24 hours and weighed to obtain the weight of collected particulate matter.

The geographic locations of the two particulate sampling stations in Hamilton are shown in Table 10 and Figure 1.

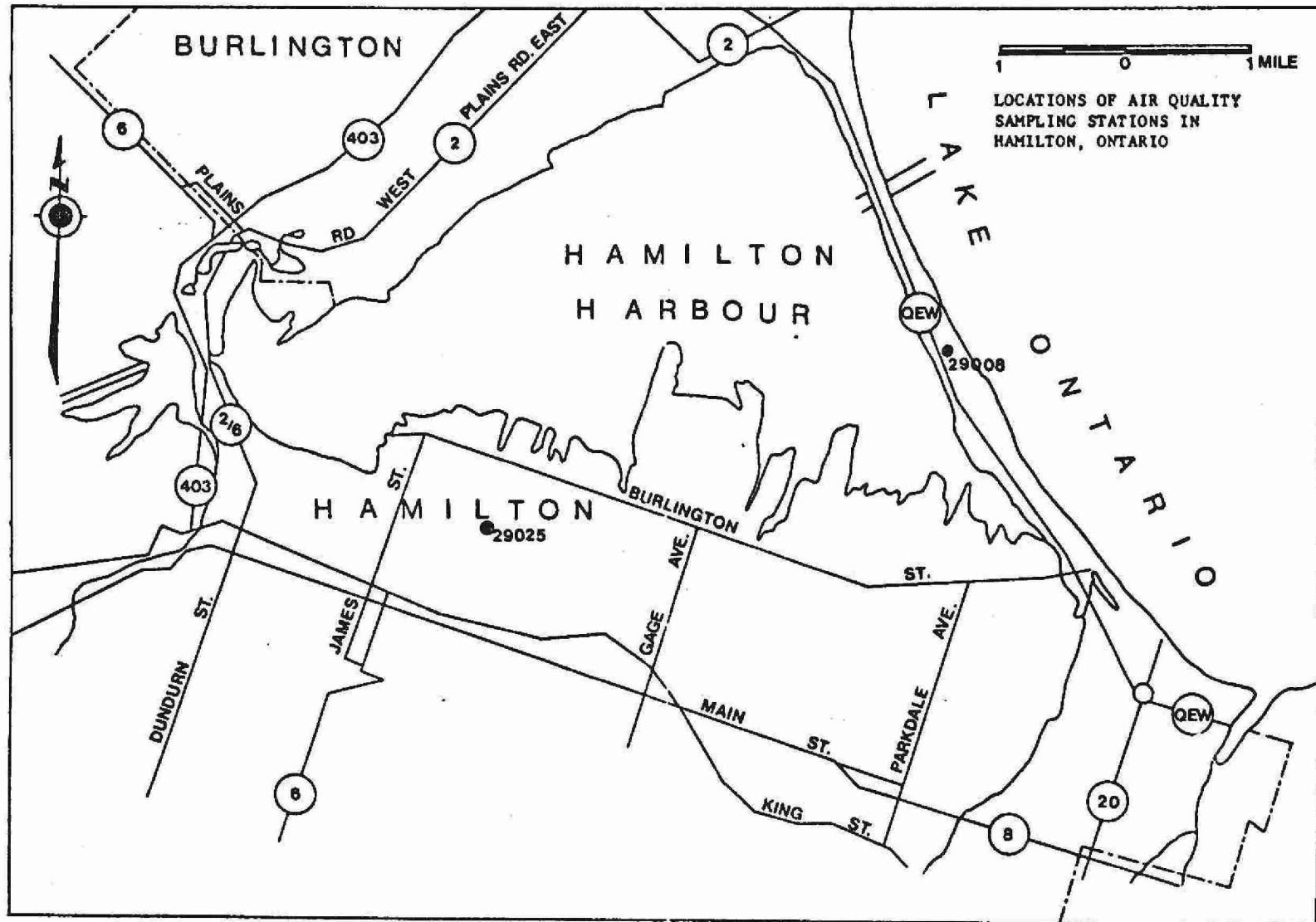
4.2 Organic Fraction Extraction

Because of the very small concentrations of PAHs in the atmosphere, it was not possible to analyze individual particulate samples. Weighed particulate-laden filters, corresponding to a specific stage of the Anderson samplers and, hence, size fraction of aerosol collected, were combined and extracted as a group. Similarly the high volume samples were also extracted on a monthly basis. As a result, average values of PAH concentrations were obtained for aerosol samples collected over a period of several particulate sampling periods and, thus, any variation in PAH-content within the specified sampling periods could not be ascertained. All particulate samples were extracted for 10 hours with 250 ml hot, redistilled spectrograde dichloromethane in a Soxhlet apparatus. The resultant dichloromethane soluble fraction (DSF) was filtered through sintered glass and the solvent reduced to a volume of 50 ml by flash evaporation at 35°C . The remaining solvent was carefully evaporated under a stream of dry nitrogen at room temperature. The residue was then dissolved in a known volume of toluene and stored at -20°C in the dark until chromatographic isolation and spectral determination of the PAH were performed.

TABLE 10. GEOGRAPHIC LOCATIONS OF AIR QUALITY SAMPLING STATIONS IN HAMILTON

STATION NO.	LOCATION OF STATION	INTERNATIONAL GRID		SITE ELEVATION ABOVE MEAN SEA LEVEL (ft)	AIR INTAKE ABOVE GROUND (ft)
		EASTING	NORTHING		
29008	North Park Hamilton	05984	47927	260	10
29025	Barton-Wentworth	05939	47900	300	12

Figure 1. Locations of air quality sampling stations in Hamilton, Ontario



5. RESULTS AND DISCUSSION

5.1 Distribution of Total Particulate Matter and Dichloromethane Soluble Fraction at Hamilton Barton Station (Site 29025)

A total of 36 high volume samples representing the sampling period June, 1977 - March, 1978 were collected at a sampling station located in the downtown area of Hamilton (Site 29025). Mean mass concentrations for particulate loading ranged from 45.5 to 141.8 $\mu\text{g}/\text{m}^3$ air during the sampling periods, while the DSF concentrations varied from 3.1 to 7.6 $\mu\text{g}/\text{m}^3$ air (Table 11). High values of particulate loading were obtained during the summer months of June, July and August, 1977. Relatively lower concentrations were found in the winter months of December, 1977, January and February, 1978. The particulate level increased to a relatively high level in March (Figure 2). Emissions due to surrounding industrial activities may have masked the "normal urban distribution pattern" of high winter-low summer particulate levels. Meteorological effects are another major factor that have complicated the study of particulate pollution in Hamilton. Due to the location and topography of the sampling stations and effects such as wind channeling, winds associated with land and lake breezes, source strength variation and other factors, the correlation of the particulate distribution with meteorological observations is exceedingly complex (21).

The monthly distribution of the dichloromethane soluble fraction obtained from the high volume samples collected at Site 29025 is shown in Figure 3.

Table 11, DISTRIBUTIONS OF SUSPENDED PARTICULATE MATTER AND
DICHLOROMETHANE SOLUBLE FRACTION COLLECTED AT
HAMILTON BARTON STATION

Month	No. of Samples	Particulate Mass* Conc. ($\mu\text{g}/\text{m}^3$)	DSF Mass Conc.** ($\mu\text{g}/\text{m}^3$)	% DSF/Particulate Matter
1977				
June	4	121.8 \pm 56.9	7.3	5.99
July	5	141.8 \pm 50.0	5.7	4.02
August	4	99.5 \pm 35.5	5.3	5.33
September	2	67.5 \pm 41.9	5.0	7.40
October	4	95.3 \pm 18.9	6.9	7.24
November	4	88.4 \pm 28.8	6.9	7.80
December	3	64.3 \pm 33.9	3.1	4.82
1978				
January	2	45.5 \pm 29.7	3.4	7.47
February	4	65.9 \pm 15.7	6.5	9.86
March	4	118.8 \pm 34.4	7.6	6.40

* Geometric Mean \pm Standard Geometric Deviation

** DSF - Dichloromethane Soluble Fraction

Figure 2 DISTRIBUTIONS OF SUSPENDED PARTICULATE
MATTER COLLECTED AT HAMILTON BARTON STATION 29025

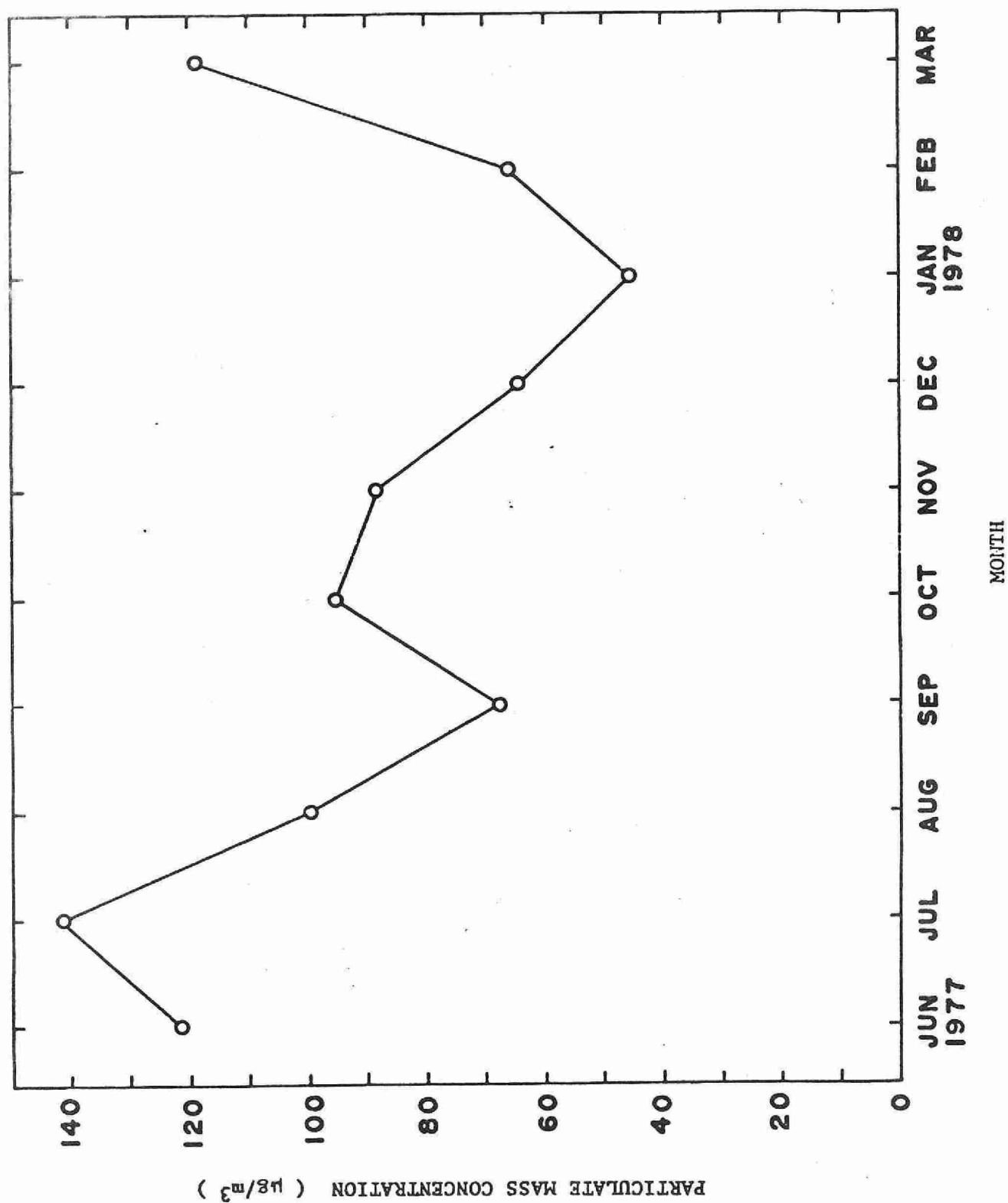
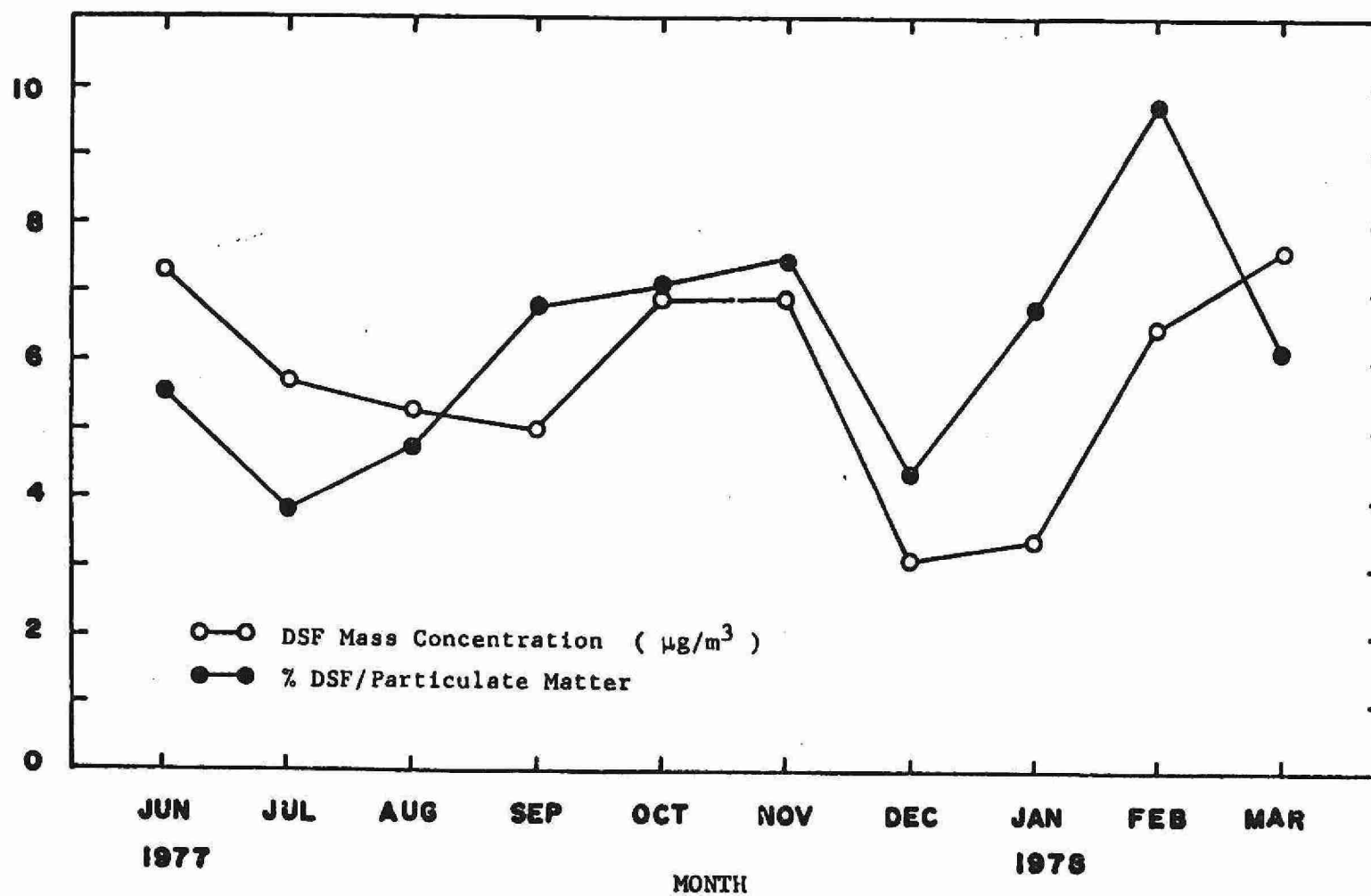


Figure 3 DISTRIBUTIONS OF DICHLOROMETHANE SOLUBLE FRACTION COLLECTED
AT HAMILTON BARTON STATION 29025



5.2 Particulate Size-Mass Distributions of Atmospheric Particulates Collected at Hamilton, West-Central Region Station (Site 29008)

In order to assess the inhalation hazards associated with a possible carcinogenic substance, it is necessary to relate the concentration of that substance to the particle size of the total suspended particulate matter. Since it has been generally accepted that particle size is a major factor in determining the toxic effects of airborne particulates, atmospheric aerosols were collected using size-selective Anderson Hi-Vol samplers at West-Central Region Station in Hamilton, Ontario. Gravimetric analysis of individual aerosol size fractions were then performed.

The common technique for representing the particle weight distribution of an aerosol calls for a determination of the relationship between the cumulative mass of the collected particulate matter and the size of that particulate matter (28). This is accomplished by plotting the logarithm of the effective cutoff diameter (ECD) for each stage on the ordinate as a function of the cumulative mass, expressed as a percent, less than or equal to the effective cutoff diameter at each stage on the abscissa. In practice, log-probability paper is used, with a standard least-squares linear regression being fit to the data.

If it is presumed that the particle size of most suspended ambient particulates follows approximately a logarithmic distribution, then the mass median diameter (MMD) may be found at the 50% mass cumulative point. The geometric standard deviation (σ_g), which is roughly equivalent to the slope of the distribution curve, provides an indication of the particle dispersion

on the range of particle sizes in an aerosol. This value is estimated from the ratio of the 84.13% value of particle size to the 50.0% value of particulate size or the 50.0% value of particle size to the 15.87% value of particle size. The size distribution curve may also be used to determine the percentage of particulate of particles less than or equal to a selected size. The actual mass concentration of particles less than or equal to a selected diameter can then be determined from the product of the percentage of the cumulative mass for that fraction and the total aerosol mass concentration.

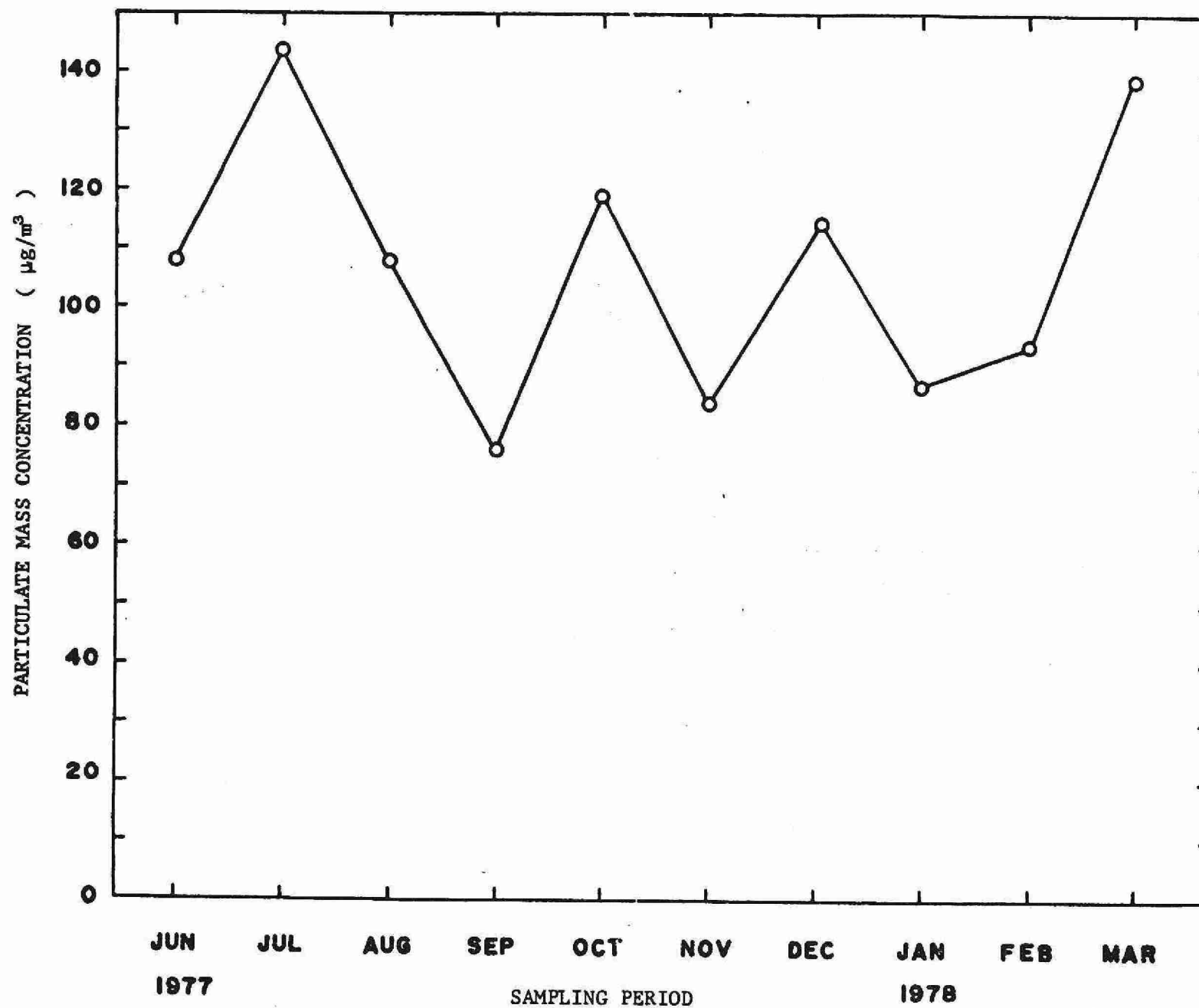
Aerosol data obtained from the sampling station location at Hamilton West-Central Region during the sampling period June, 1977 - March, 1978 are detailed in Table 12. The data presented include the total aerosol mass concentration, MMD, σ_g , and percentage of particles less than or equal to 1.0 μm and 3.0 μm diameters. The geometric mean values, together with the standard geometric deviations, were computed using statistical techniques. In this case, the standard geometric deviation represents the spread of values over the number of samples analysed and, thus, gives an indication of the degree of variability for different sampling periods.

The total aerosol mass concentration, displayed in Figure 4, exhibited a variable distribution that may be explained, at least in part, by seasonal factors. The maximum mass concentration occurred in the summer months of June, July and August, 1977, but relatively high levels occurred also in October, December, 1977 and March, 1978. Considerable fluctuations were observed in the monthly particulate distribution. This may be due to meteorological factors such as prevailing wind direction and wind speed,

Table 12. DISTRIBUTIONS OF SUSPENDED PARTICULATE MATTER
COLLECTED AT HAMILTON WEST-CENTRAL STATION

Geometric Mean \pm Standard Geometric Deviation						
Month	No. of Samples	Particulate Mass Conc. ($\mu\text{g}/\text{m}^3$)	MMD μm	σ_g	Conc. $\leq 1.0 \mu\text{m}$ (%)	Conc. $\leq 3.0 \mu\text{m}$ (%)
1977						
June	5	108.0 \pm 48.3	2.7 \pm 0.2	6.2 \pm 2.5	28.1 \pm 2.5	52.3 \pm 2.2
July	5	143.8 \pm 24.7	2.9 \pm 0.4	10.2 \pm 2.5	27.8 \pm 2.6	50.3 \pm 2.7
August	5	108.8 \pm 27.7	3.5 \pm 0.9	16.0 \pm 9.7	25.7 \pm 3.1	47.5 \pm 4.8
September	4	76.7 \pm 75.1	3.4 \pm 1.7	23.1 \pm 21.6	27.6 \pm 10.6	47.3 \pm 8.4
October	4	119.8 \pm 47.2	2.6 \pm 0.9	15.6 \pm 5.6	32.6 \pm 5.5	52.2 \pm 5.6
November	4	84.2 \pm 42.3	4.0 \pm 2.1	20.8 \pm 16.4	23.6 \pm 7.3	44.6 \pm 7.8
December	4	114.3 \pm 58.0	4.1 \pm 3.2	27.6 \pm 47.2	27.0 \pm 5.8	45.4 \pm 7.7
1978						
January	3	86.8 \pm 54.5	1.3 \pm 2.1	9.8 \pm 6.8	31.1 \pm 26.9	55.7 \pm 17.0
February	4	93.8 \pm 50.6	1.9 \pm 1.4	11.1 \pm 4.8	33.8 \pm 15.6	55.0 \pm 12.5
March	4	139.1 \pm 48.5	2.7 \pm 0.8	11.3 \pm 5.2	29.2 \pm 6.7	52.3 \pm 6.4

Figure 4. DISTRIBUTIONS OF SUSPENDED PARTICULATE MATTER
COLLECTED AT HAMILTON WEST-CENTRAL STATION 29008



incidence of stable atmospheric conditions and rates of emissions from specific sources.

The mass median diameter of suspended particulates varied between 2.6 and 3.5 μm during the monthly periods of June - October, 1977, rising to 4.1 in December 1977 and decreasing to 1.3 in January 1978 (Table 12). The primary maxima in the value of MMD's of the atmospheric aerosols occurred in November, December, 1977 (Figure 5).

The relatively low values of σ_g during the periods June and July, 1977, January - March, 1978, reflected the homogeneity of the sampled aerosols. However in September, November and December, 1977, a significant increase in σ_g was observed. This fluctuation of the distribution reflected an increase in the heterogeneity of the suspended particulate matter.

The monthly variation in the fractional content of the aerosol mass represented by particles of diameter less than or equal to 1.0 μm and 3.0 μm is illustrated in Figure 6. In general, 24 to 34 percent of the aerosol mass was found in particles of 1.0 μm diameter or less, while 45 to 56 percent of the aerosol mass was found in particles of diameter 3.0 μm or less. The respirable fraction of the particulate mass remained relatively constant throughout the sampling period with only minor variations.

The monthly distribution of the dichloromethane soluble fraction obtained from particulate of size less than or equal to 1.1 μm and from particulate with size range from 1.1 - 2.0 μm by Soxhlet extracting Anderson Hi-Vol samples collected at Hamilton Site 29008 is shown in Table 13. The graphical representations are illustrated in Figure 7 and Figure 8.

Figure 5. MONTHLY VARIATION OF MMD AND σ_g AT HAMILTON (WEST-CENTRAL STATION, SITE 29008)

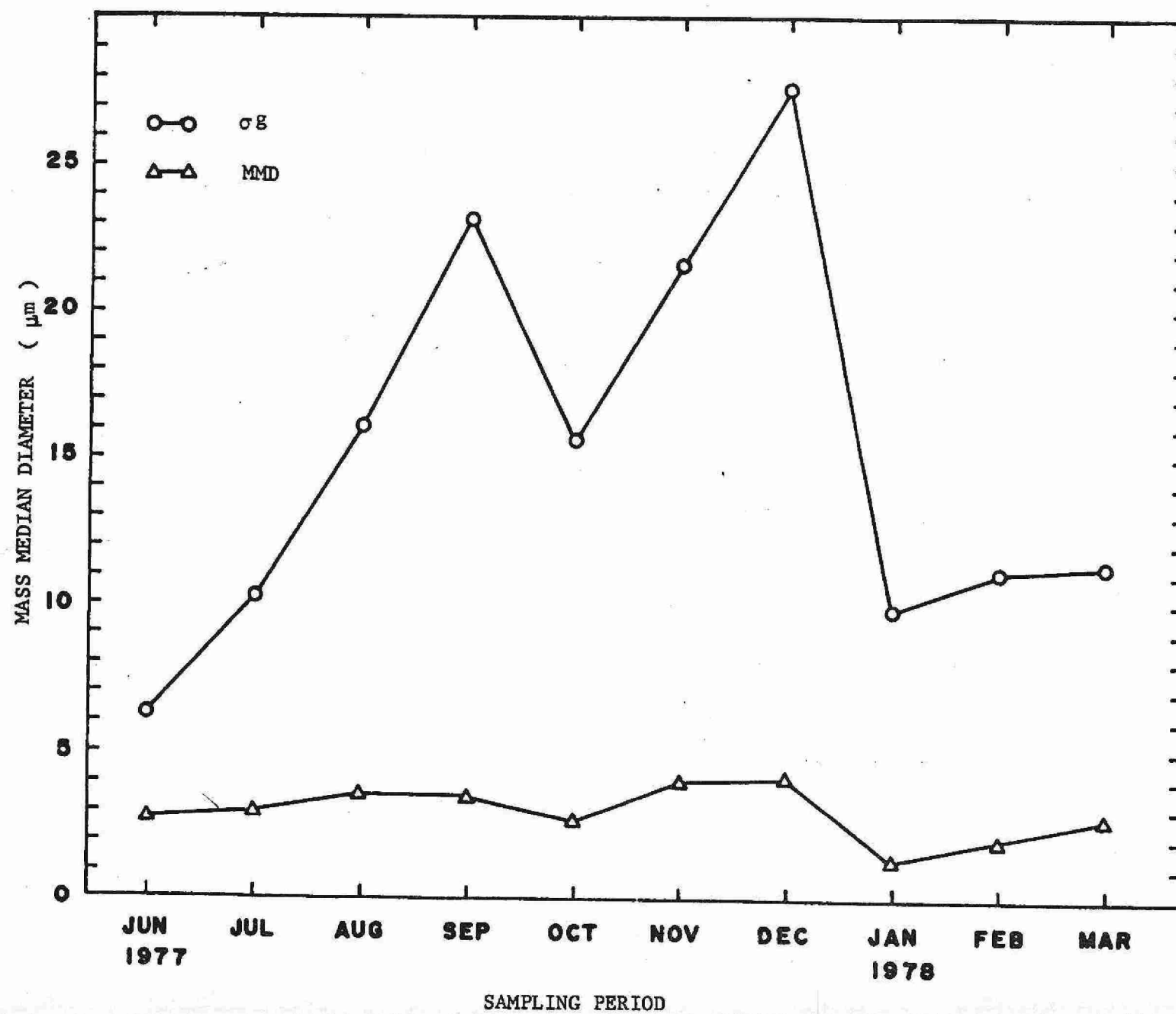


Figure 6. MONTHLY VARIATION OF PERCENT MASS $\leq 1.0 \mu\text{m}$ AND $\leq 3.0 \mu\text{m}$ AT HAMILTON (SITE 29008)

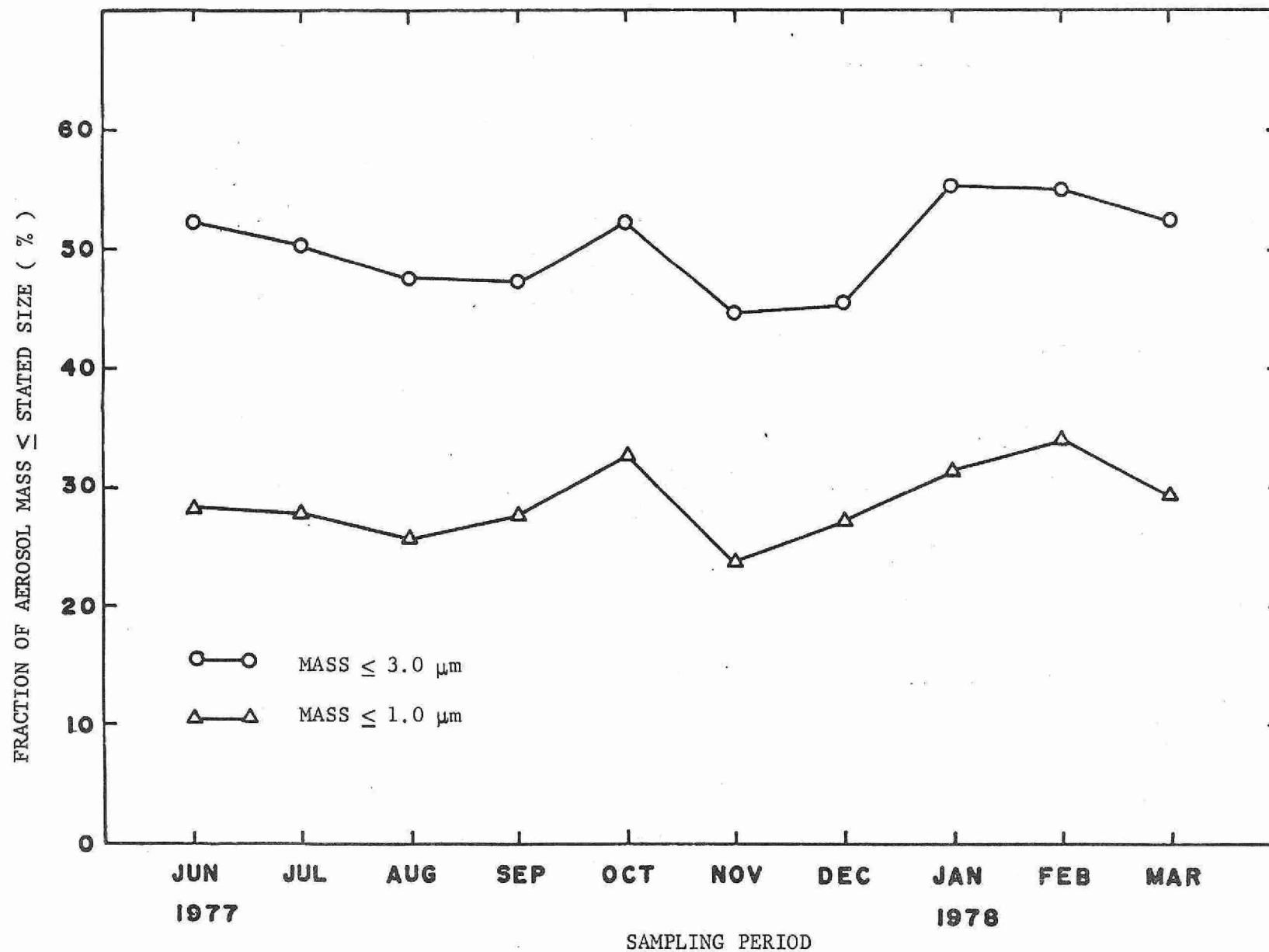


Table 13. DISTRIBUTIONS OF VARIOUS SIZES SUSPENDED
PARTICULATE MATTER AND DICHLOROMETHANE SOLUBLE
FRACTION COLLECTED AT HAMILTON WEST-CENTRAL STATION

(Geometric Mean \pm Standard Geometric Deviation)

Month	No. of Samples	Size: $\leq 1.1 \mu\text{m}$ ($\mu\text{g}/\text{m}^3$)			Size: $1.1 - 2.0 \mu\text{m}$ ($\mu\text{g}/\text{m}^3$)		
		Particulate Mass Conc.	DSF	%DSF/Part.	Particulate Mass Conc.	DSF	%DSF/Part.
1977							
June	5	32.9 \pm 15.8	4.7	14.3	13.3 \pm 5.8	6.3	47.4
July	5	43.1 \pm 8.3	8.8	20.4	16.6 \pm 2.9	4.5	27.1
August	5	30.2 \pm 11.8	5.9	19.5	12.2 \pm 4.0	4.9	40.2
September	4	23.4 \pm 31.7	6.3	26.9	7.1 \pm 8.3	4.8	67.6
October	4	42.0 \pm 19.8	5.3	12.6	11.3 \pm 1.4	6.2	54.9
November	4	22.2 \pm 9.6	3.6	16.2	8.9 \pm 4.9	3.9	43.8
December	4	31.7 \pm 22.2	3.0	9.5	12.6 \pm 3.9	3.5	27.8
1978							
January	3	31.3 \pm 14.8	5.6	17.9	7.4 \pm 8.7	1.8	24.3
February	4	32.9 \pm 9.3	3.7	11.2	10.6 \pm 8.3	3.8	35.8
March	4	41.3 \pm 22.2	5.7	13.8	21.6 \pm 7.6	3.9	18.1

FIGURE 7. DISTRIBUTIONS OF SUSPENDED PARTICULATE MATTER OF SIZE LESS THAN OR EQUAL TO $1.1 \mu\text{m}$ AND DICHLOROMETHANE SOLUBLE FRACTION COLLECTED AT HAMILTON WEST-CENTRAL STATION

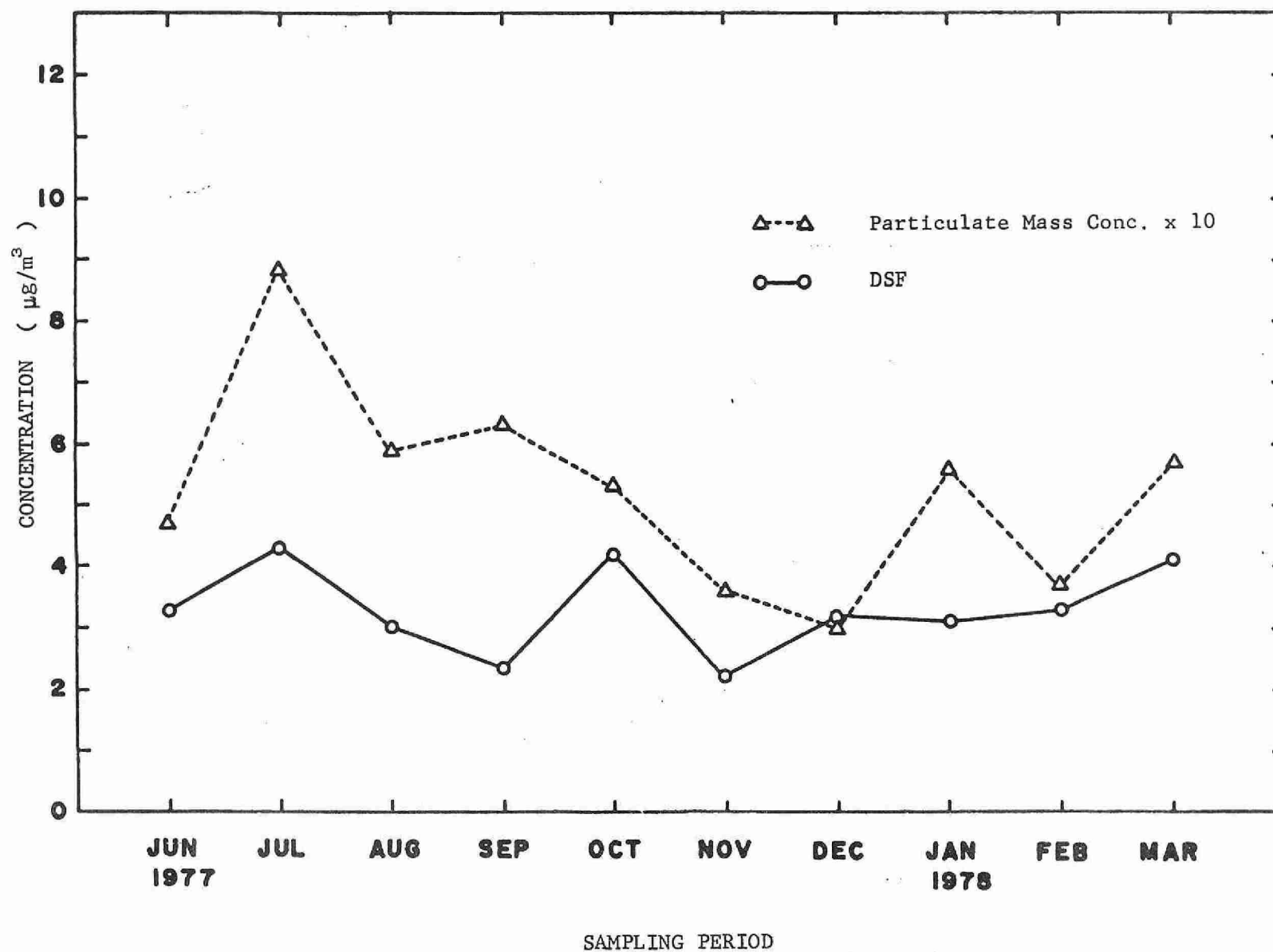
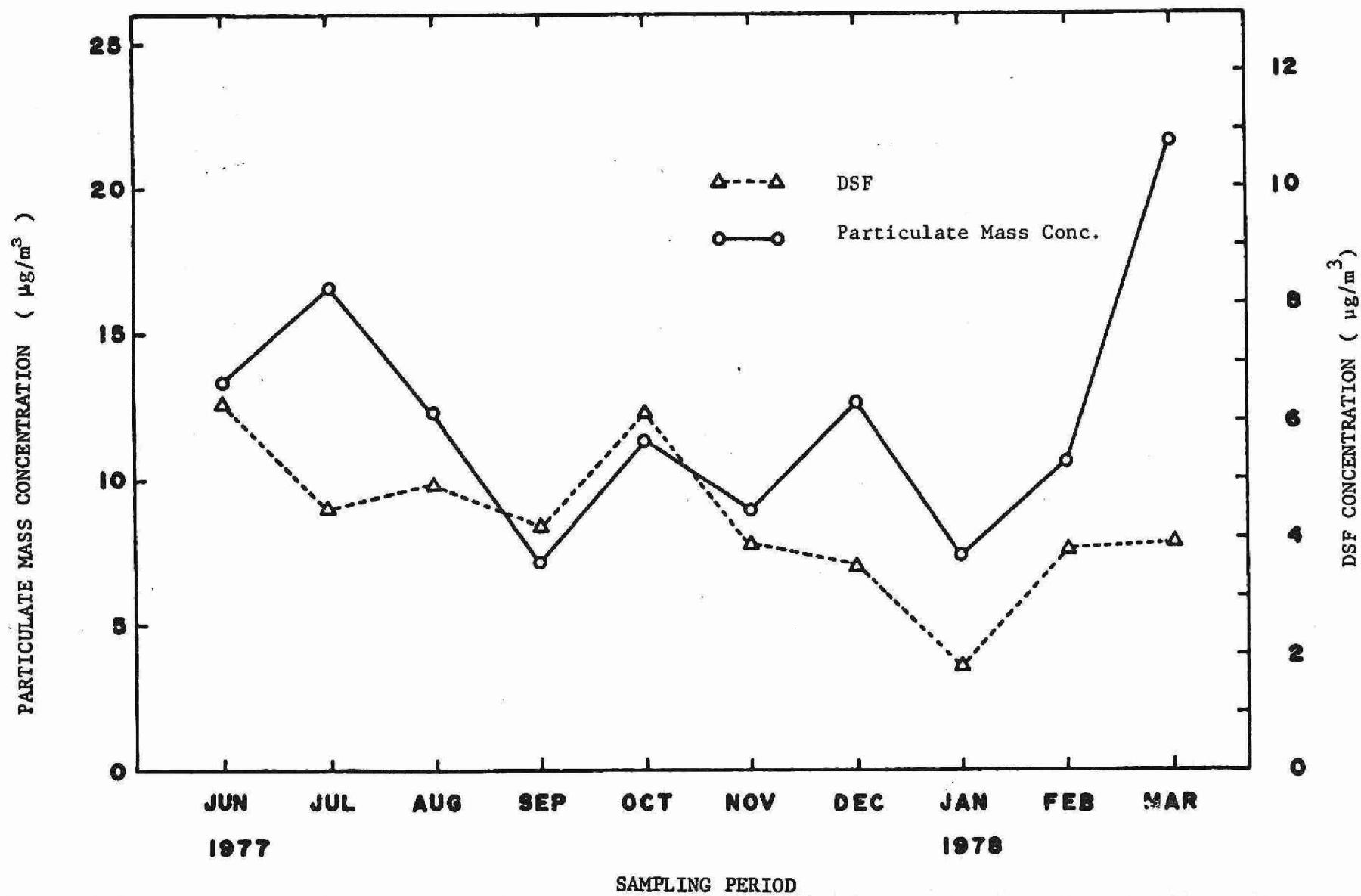


Figure 8. DISTRIBUTIONS OF SUSPENDED PARTICULATE MATTER OF SIZE: 1.1 - 2.0 μm
AND DICHLOROMETHANE SOLUBLE FRACTION COLLECTED AT HAMILTON WEST-CENTRAL STATION



In terms of $\mu\text{g DSF}/\text{m}^3$ air, considerable variations were observed in both size groups of particulates. It appeared that DSF concentrations are higher in the June-October months and lower in the winter months. In the particulate group of size less than or equal to $1.1 \mu\text{m}$, DSF with respect to m^3 of air attained a maximum in July of about three times that observed in December. In the particulate group of size ranging from $1.1 \mu\text{m}$ to $2.0 \mu\text{m}$, the concentration of DSF in the period June-October was approximately 1.6 times greater than that of the cold months of November through March. Comparison of the monthly DSF concentrations in both size groups revealed significant differences in most months of the ten-month period. Expressing the concentrations of DSF in terms of percent particulate, it would appear that the percentages of DSF in size group $1.1 - 2.0 \mu\text{m}$ (18.1 - 67.6%) are generally more than twice as high as the percentages obtained from the size group $\leq 1.1 \mu\text{m}$ (9.5 - 26.9%).

6. PAH Distribution in Relation to Particle Size of Hamilton Samples

The organic extracts (DSF) of the particulate samples discussed in Section 5 are in process of analysis for PAH content. To date, analytical data are available for benzo(a)pyrene (BaP), benzo(k)fluoranthene (BkF) and perylene (Per) for each month from June through December 1977, in the particle size range less than or equal to $1.1 \mu\text{m}$. The results for BaP are presented in Table 14. Relatively high concentrations of this carcinogen/mutagen were found in October and December samples of this small, respirable size range,

The highest concentrations of BkF also occurred in samples $\leq 1.1 \mu\text{m}$ collected in October and December, as shown in Table 15.

Table 14. DISTRIBUTIONS OF BENZO(a)PYRENE ASSOCIATED WITH PARTICULATES THAT ARE LESS THAN OR EQUAL TO 1.1 MICRON COLLECTED AT HAMILTON NORTH PARK STATION

MONTH	CONCENTRATION OF BENZO(a)PYRENE *		
	ng/1000 m ³ air	ng/mg of particulate less than or equal 1.1 micron	ng/mg of total particulate sampled
<u>1977</u>			
June	473.5	14.38	4.38
July	607.4	14.09	4.22
August	502.2	16.63	4.62
September	529.2	22.62	6.90
October	2344.6	55.83	19.57
November	827.0	37.25	9.82
December	1278.5	40.30	11.18

*Concentrations have been corrected by calibration against standard

Table 15. Distribution of Benzo(k)fluoranthene Associated with Particulates of Size Equal to or Less than 1.1 micron, Collected at Hamilton North Park Station

Month 1977	Concentration of Benzo(k)Fluoranthene [*]		
	ng/1000 m ³ air	ng/mg of particulate ≤ 1.1 μm	ng/mg of total particulate sampled
June	231.9	7.05	2.15
July	520.8	12.08	3.62
August	454.6	15.05	4.18
September	700.6	29.94	9.13
October	1716.1	40.86	14.32
November	707.4	31.86	8.40
December	868.4	27.39	7.60

* Concentrations have been corrected by calibration against standard

Concentrations of Per were considerably lower than those of BaP or BkF (Table 16), although maximal concentrations also occurred in October and December.

More information on the distribution of PAH in the Hamilton samples, in relation to particle size, will be presented at a later date when this analytical programme has been completed.

Table 16. DISTRIBUTIONS OF PERYLENE ASSOCIATED WITH PARTICULATES THAT ARE LESS THAN OR EQUAL TO 1.1 MICRON COLLECTED AT HAMILTON NORTH PARK STATION

MONTH	CONCENTRATIONS OF PERYLENE*		
	ng/1000 m ³ air	ng/mg of particulate less than or equal 1.1 micron	ng/mg of total particulates sampled
<u>1977</u>			
June	90.1	2.74	0.83
July	142.5	3.31	0.99
August	109.3	3.62	1.00
September	150.8	6.44	1.97
October	551.9	13.14	4.61
November	199.3	8.98	2.37
December	326.5	10.30	2.86

* Concentrations have been corrected by calibration against standard

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The Photomodification of Polycyclic Aromatic Hydrocarbons (PAH)
in the Solid State under Simulated Atmospheric Sunlight Conditions

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) have long been found in varying concentrations in the atmosphere of cities and towns throughout the world. Because of their carcinogenic activity, they belong to the most intensely studied mixtures of industrial emission products which come in contact with the human organism (1). During recent years, the studies of metabolism of PAH have greatly increased (2-9), as it is known that PAH may not be carcinogenic intrinsically but may transform into active intermediates which create a possible health hazard. The same thing is true with photochemical reactions of PAH. Since many of these substances react with the natural or pollutant components of the atmosphere, such reactions may convert relatively innocuous pollutants into substances which constitute a potential cancer hazard. The study of the modification of such airborne arenes by environmental factors is therefore very important as it may provide an explanation of possible reduction or enhancement of the biological effect on humans. Moreover, the data obtained from such studies may lead to a better interpretation of the quantities of these substances present in the atmosphere.

Most of the earlier research conducted in this area was concerned with the photooxidation and photoozonation of arenes in solution (10-22). However, the mechanism and reaction rates of such liquid phase oxidation is by no means similar to a gas-solid type of reaction that will occur in the atmosphere.

In recent years there have been a number of attempts to study the modification of polycyclic aromatic hydrocarbons (PAH) under simulated atmospheric conditions. Falk et al. (30) dissolved various PAH in lipid solvents and applied them to Watman filter paper. The filter papers were exposed to various conditions including a synthetic smog which had an oxidant content of approximately 30 ppm as determined by the potassium iodide method. Tebbens et al. (24-26) produced a smoke through the incomplete combustion of propane and passed the smoke through a 22-foot long, 6-inch diameter pyrex pipe, the first half of which was irradiated with banks of fluorescent lamps. The smoke was analysed at both ends of the pipe for its PAH content. Spicer and Jones (31) determined the carbon balance of aromatic hydrocarbons in a photochemical smog system.

These methods, while yielding interesting information, are not really representative of actual atmospheric conditions. Oxidant levels of 30 ppm do not occur and fluorescent lamps produce line spectra which are in no way analogous to the solar spectrum. What is required, therefore, is a system which will expose PAH, under controlled conditions, to normal atmospheric irradiation, oxidant levels, temperature and pressure. Above all, heterogeneous contact between the PAH and gases in the reaction system should exist. In this work a dynamic flow reactor system was employed for studying gas-solid reactions in which atmospheric conditions were more closely duplicated. This system and the simulated sunlight source of irradiation has been described by Lane and Katz (32).

2. EXPERIMENTAL METHODS

2.1 Apparatus

The apparatus consists of an air source, air purification train, ozone generator, reaction chamber and irradiation source and is shown schematically in Figure 1.

Air from a cylinder (Matheson Zero gas) was passed through a Gelman glass fiber filter to remove oil droplets and solid particles which might be introduced into the air stream. A needle valve controlled the flow of air to a purification train which consisted of absorbing towers of activated charcoal, magnesium perchlorate and ascarite. A calibrated rotameter measured the air flow to the ozone generator and, hence, to the reaction chamber. All connections downstream of the needle valve were borosilicate glass to glass, or glass to teflon to glass.

The ozone generator was fabricated in this laboratory after the design of Hodgeson et al. (36) and was calibrated by the neutral buffered potassium iodide method with an air flow of 100 ml per minute through the generator. A constant voltage transformer regulated the power supply which powered the Pen Ray UV lamp used in the generator.

The reaction flask was a 20 liter glass jar with an air inlet stopcock at the bottom and an air outlet stopcock diametrically opposite but at the top of the jar. Extruded silicone polymer (6.35 mm x 6.35 mm) was sealed to the top of the jar with silicone glue to form a gasket. After 12 months of use, there has been no detectable reaction between the silicone polymer and the ozone used in the reactor. A 3.18 mm thick borosilicate

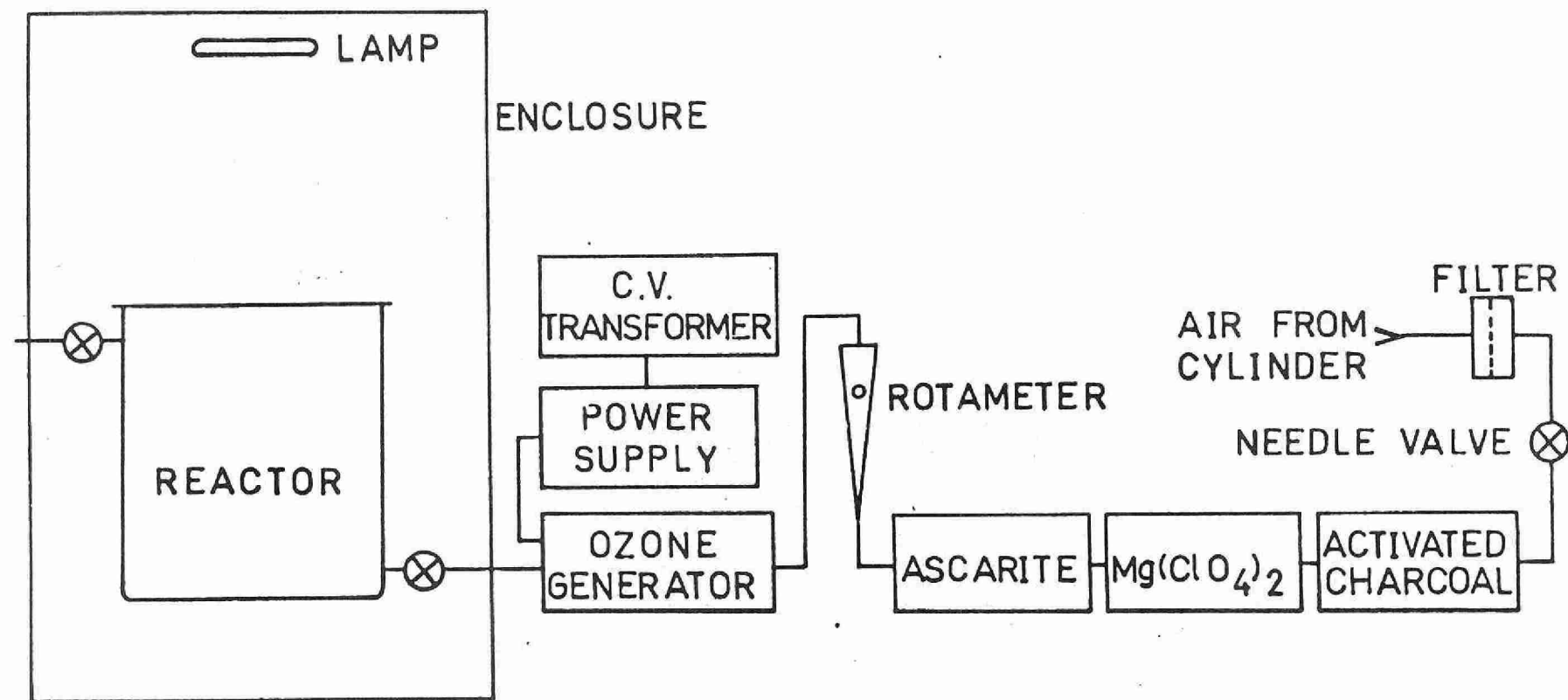


Figure 1

(pyrex) disc covered the top of the reactor and acted as a filter for the irradiation source. Reaction dishes were placed on a support produced from glass rods. The glass support was 6.5 cm above the air inlet and gave maximum support to the dishes, while presenting minimum resistance to air flowing through the reactor.

Both the reaction chamber and irradiation source were placed inside an enclosure to exclude laboratory fluorescent illumination from the reaction. A temperature build-up was minimized by installing a muffin fan at the top of the enclosure.

A 500 watt General Electric Quartzline lamp (Q500T3/CL) mounted in a standard photographic housing, 46 cm above the dishes in the reactor, was used as the irradiation source. The spectral output of the lamp was obtained using a Heath 701 spectrophotometer equipped with a 1P-28 photomultiplier tube. Actinic irradiance measurements were made using the standard uranyl nitrate-oxalic acid method and current readings were taken using a number 935 photodiode tube enclosed in a black box with a slit opening of 1.6 mm by 3.18 mm. Both actinic irradiance and current tests were made for the lamp, background irradiation and natural sunlight. When lamp and background irradiation tests were carried out, a 3.18 mm pyrex filter was placed over the uranyl nitrate-oxalic acid absorbing solutions and over the slit on the phototube housing. No pyrex filter was used when making sunlight measurements.

To our knowledge, this is the first time that a Quartzline lamp has been used to simulate sunlight in photochemical reactions. Figure 2 shows the spectral output of the sun at solar zenith angles of 40° and 60° ,

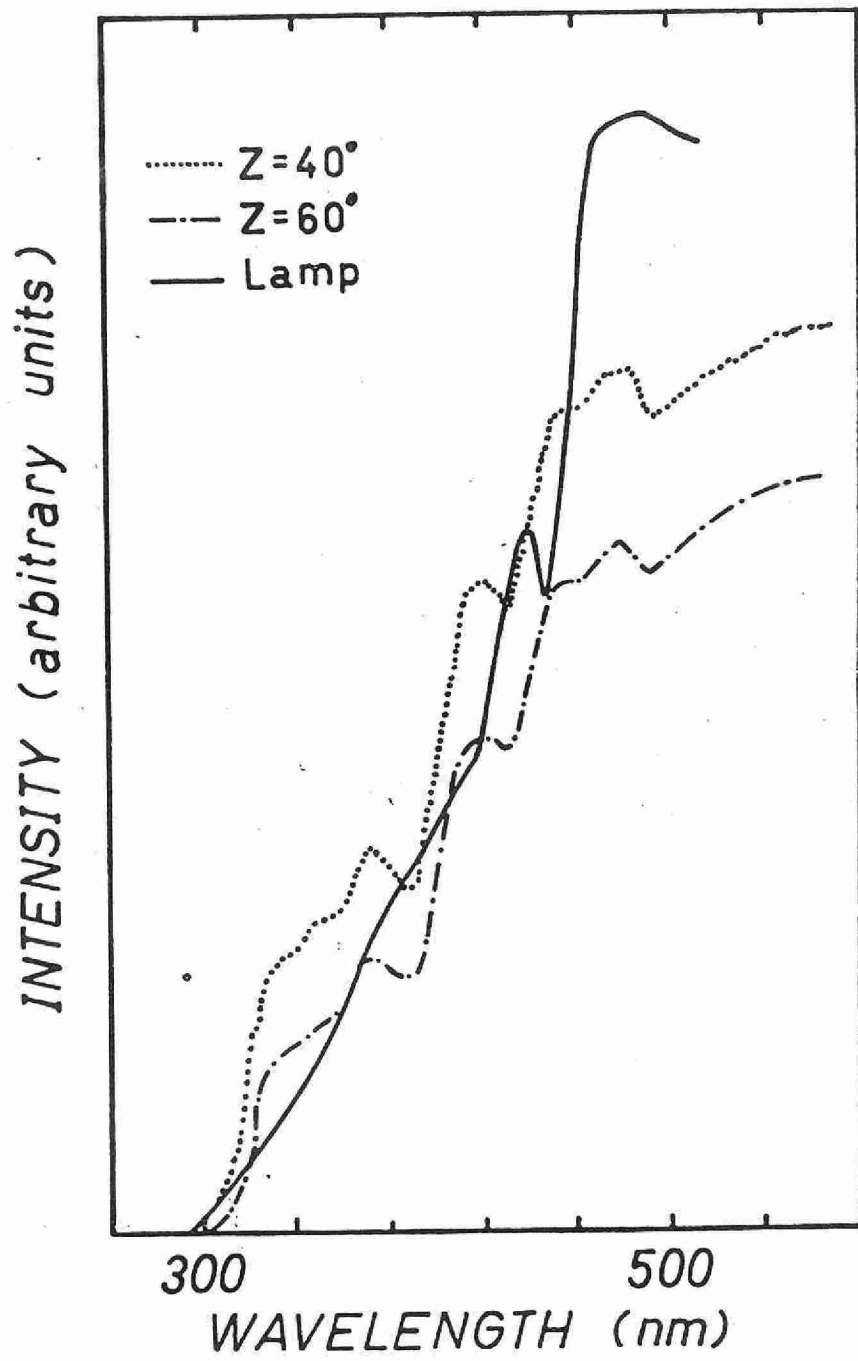


Figure 2

as reported by Leighton (37). The spectral distribution of the Quartzline lamp using a 3.18 mm pyrex disc as a filter is also shown but not to the same absolute intensity scale. It is important to note that the spectral distribution of the Quartzline lamp is a continuous spectrum, not a line spectrum, as is the case with fluorescent and sun lamps, and that its spectrum very closely resembles that of the sun between 2950 Å and 5000 Å.

Actinic irradiance and current measurements were made at a point 46 cm below the lamp to compare the lamp emission with background radiation, both inside and outside the enclosure, and with sunlight. The results are summarized in Table I. As can be seen, fluorescent lighting in a room could contribute significantly to the reaction if it were not excluded, for it is about 2% of the actinic irradiance of the lamp. Background irradiation inside the enclosure is insignificant. This lamp is, therefore, considered to be an excellent inexpensive laboratory source for simulating sunlight. Wavelengths down to 2300 Å may be obtained if the pyrex filter is omitted.

3. SAMPLE PREPARATION AND REACTION

In earlier experiments, dilute solutions of about 1.0 µg/ml of benzo(a)pyrene and other PAH in spectrograde n-hexane were transferred by Eppendorf pipet to each of twelve petri dishes, 5 cm in diameter. The PAH solution was made to coat the bottom of each petri dish as evenly as possible, while carefully evaporating the hexane at room temperature under a stream of nitrogen. However, difficulty was experienced in obtaining an even coating of PAH on the petri dishes. Occasionally, several spots of

TABLE I. Light Intensity Comparison

Irradiation tested	Actinic irradiance (photons, sec ⁻¹)	Current (amperes)
Direct sunlight	7.26×10^{16}	2.95×10^{-5}
Quartzline lamp output filtered by the .32 cm pyrex filter	3.97×10^{15}	2.10×10^{-6}
Background - laboratory fluorescent irradiation	7.03×10^{13}	4.4×10^{-8}
Background - inside reactor enclosure	--	$\sim 4 \times 10^{-11}$

multilayers would be formed and these spots introduced variations in replicate photooxidation experiments. The variability was probably due to more rapid decomposition of the upper layers and the products served to protect the inner layers from further oxidation. It was decided therefore to use thin-layer chromatographic plates (TLC).

Brinkman Cellulose MN 300 precoated TLC plates were used as a coating medium for the PAH. Unlike silica gel plates which showed changes in the presence of PAH (33-34), cellulose plates had no effect with the PAH under study. The dimensions (20 x 20 x 0.01 cm) furnished an excellent surface for exposure to irradiation. Stock solutions of 90-100 µg/ml of 1,2-benzanthracene (benz(a)anthracene), 4-5-benzpyrene (benzo(e)pyrene), 1,2,3,4-dibenzanthracene (dibenz(a,c)anthracene) and 1,2,5,6-dibenzanthracene (dibenz(a,h)anthracene) were dissolved in glass-distilled chloroform. Each of the prepared solutions was transferred to two 10 ml volumetric flasks and filled up to the mark. These solutions were stored in the dark as standards and analyzed to check the initial concentration of the PAH. 100 ml portions of each stock solution were transferred to a TLC developing tank. Five precoated plates were put inside the tank at one time until the solution ran up to 1.0 cm from the top of the plates. The plates were then taken out, air-dried in the dark and the upper 2.5 cm of coating material was removed. They were then placed in the reaction chamber, one at a time, and exposed for definite periods of time under the following conditions:

- i) simulated sunlight (by irradiation)
- ii) simulated sunlight and 0.2 ppm ozone
- iii) 0.2 ppm ozone in the dark

The reaction chamber, during irradiation with the quartzline lamp or in the experiments conducted in the dark, was supplied with filtered, purified air at a flow rate of 1.3 litres per minute, measured by a calibrated rotameter.

After irradiation, the remaining coating material on the TLC plates was carefully removed and extracted several times with glass-distilled chloroform. The extract, a pale yellow solution, was then concentrated to about 5 ml in a rotary evaporator and finally evaporated to dryness under a stream of nitrogen. These prepared samples were kept in the dark. Just before analysis by high pressure liquid chromatography (HPLC), exactly 2 ml of distilled chloroform was added to the extract which was then injected immediately into the HPLC.

In order to avoid interference from the photooxidation products, the decrease in concentration of the parent PAH was detected using a Water Associates 6000A Liquid Chromatograph equipped with a fixed wavelength (254 nm) UV detector, refractive index detector and a Varian Fluorichrom detector. An ODS Spherisorb Column was used to separate the products and determine the rate of photooxidation. Actually HPLC offers many advantages over GC and other analytical instruments in PAH analysis; it operates at ambient temperature, the reversed phase packings are highly selective for separation of isomeric PAH, the eluted fraction can be collected for further analysis and baseline separation of the PAH is easily accomplished.

The optimum operating conditions for HPLC were determined empirically by adjusting the amount of methanol in the mobile phase and the

liquid flow rate. The best separation for the samples, using the ODS Sperhisorb column, was obtained with 20% H₂O - 80% MeOH and a flow of 0.8 ml/min.

Oxidation or irradiation experiments with ozone were conducted at a concentration of 0.2 ppm ozone in air, as measured by the neutral, buffered potassium iodide method and checked by a Dasibi Model 1003 AH Ozone analyzer. Such ozone concentration is commonly detected in a highly polluted urban atmosphere (35).

4. RESULTS

As shown by the data in Table 2, the two isomeric dibenzanthracenes showed a similar pattern of decomposition. 1,2,3,4-dibenzanthracene showed a half-life of 9.2 hrs. when irradiated by simulated sunlight and 4.6 hours with simulated sunlight irradiation in the presence of 0.2 ppm of ozone. 1,2,5,6-dibenzanthracene showed a half-life of 9.6 hrs. with irradiation and 4.8 hrs. when subjected to both irradiation and 0.2 ppm of ozone. The rates of oxidation under both simulated sunlight and ozone were approximately twice that of the rate with sunlight alone,

Graphical plots of the percent decomposition with time in hours for these two isomeric dibenzanthracenes are presented in Figures 3-6. The log decomposition rate versus time plots are shown in Figures 7 and 8. With irradiation alone, the curves show a pseudo first order rate of decomposition (Fig. 7). This rate approaches more nearly a first order reaction in the case of irradiation in the presence of 0.2 ppm ozone (Fig. 8).

TABLE 2. The % Decomposition and Half-life of the PAH

<u>Time (hrs.)</u>	<u>1,2,3,4-Dibenzanthracene</u>		<u>1,2,5,6-Dibenzanthracene</u>	
	<u>Sunlight + O₃ (0.2 ppm)</u>	<u>Sunlight</u>	<u>Sunlight</u>	<u>Sunlight + O₃ (0.2 ppm)</u>
0	0	0	0	0
1	16.5	4.5	-	-
2	29.4	14.2	17.5	26.2
3	43.5	18.3	-	-
4	48.2	29.0	30.7	43.9
5	54.7	-	27.0	-
6	58.2	41.5	38.8	57.1
8	62.0	47.5	39.9	60.5
10	79.0	53.3	52.0	70.2
12	-	58.8	57.6	-
14	80	63.4	-	81
16	-	67.0	-	-
18	87.0	-	62.5	-
Half-life, t _{1/2} (hours)	4.6	9.2	9.6	4.8

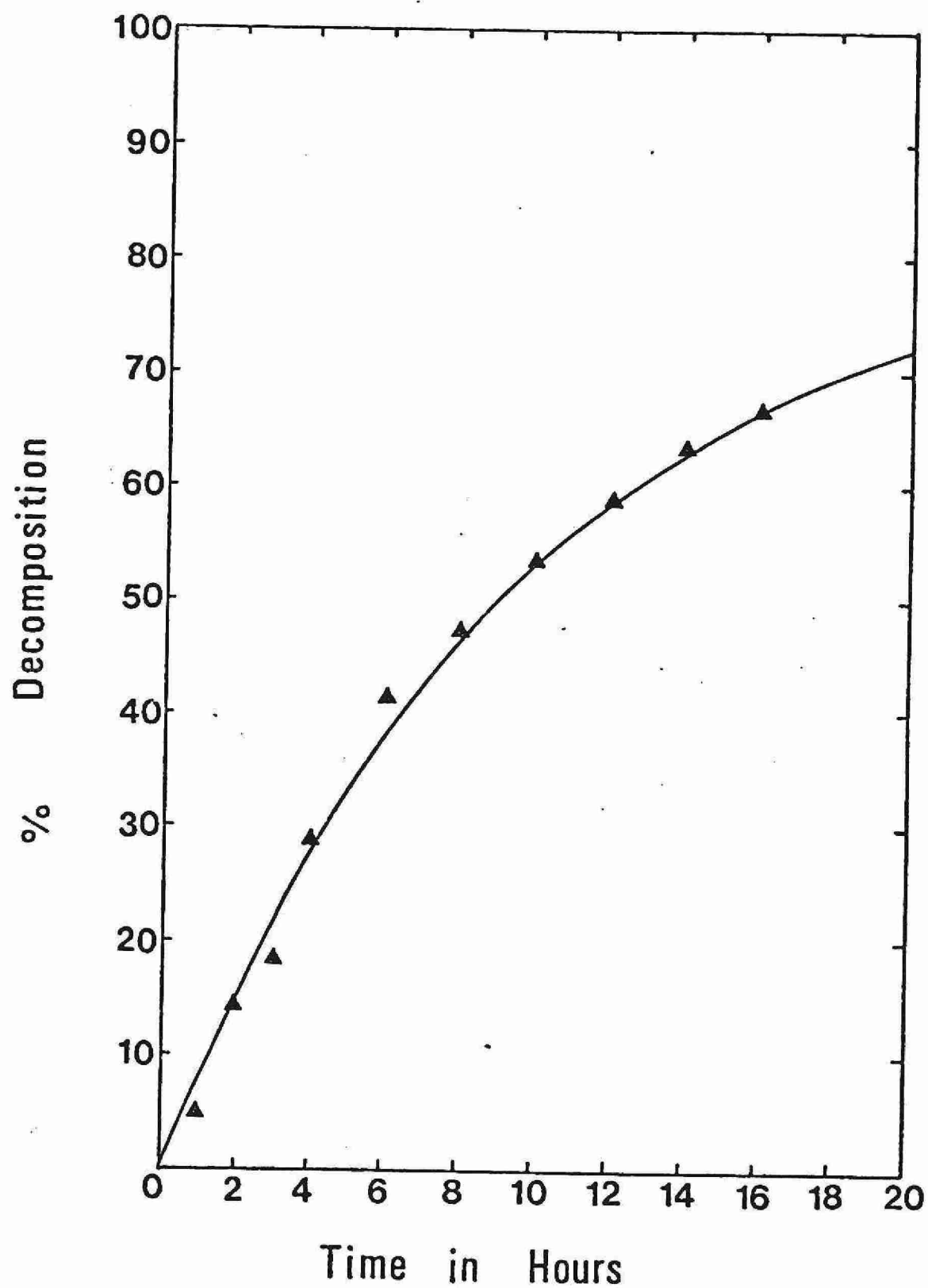


FIGURE 3. THE MODIFICATION OF 1,2,3,4-DIBENZANTHRACENE
UNDER SIMULATED SUNLIGHT

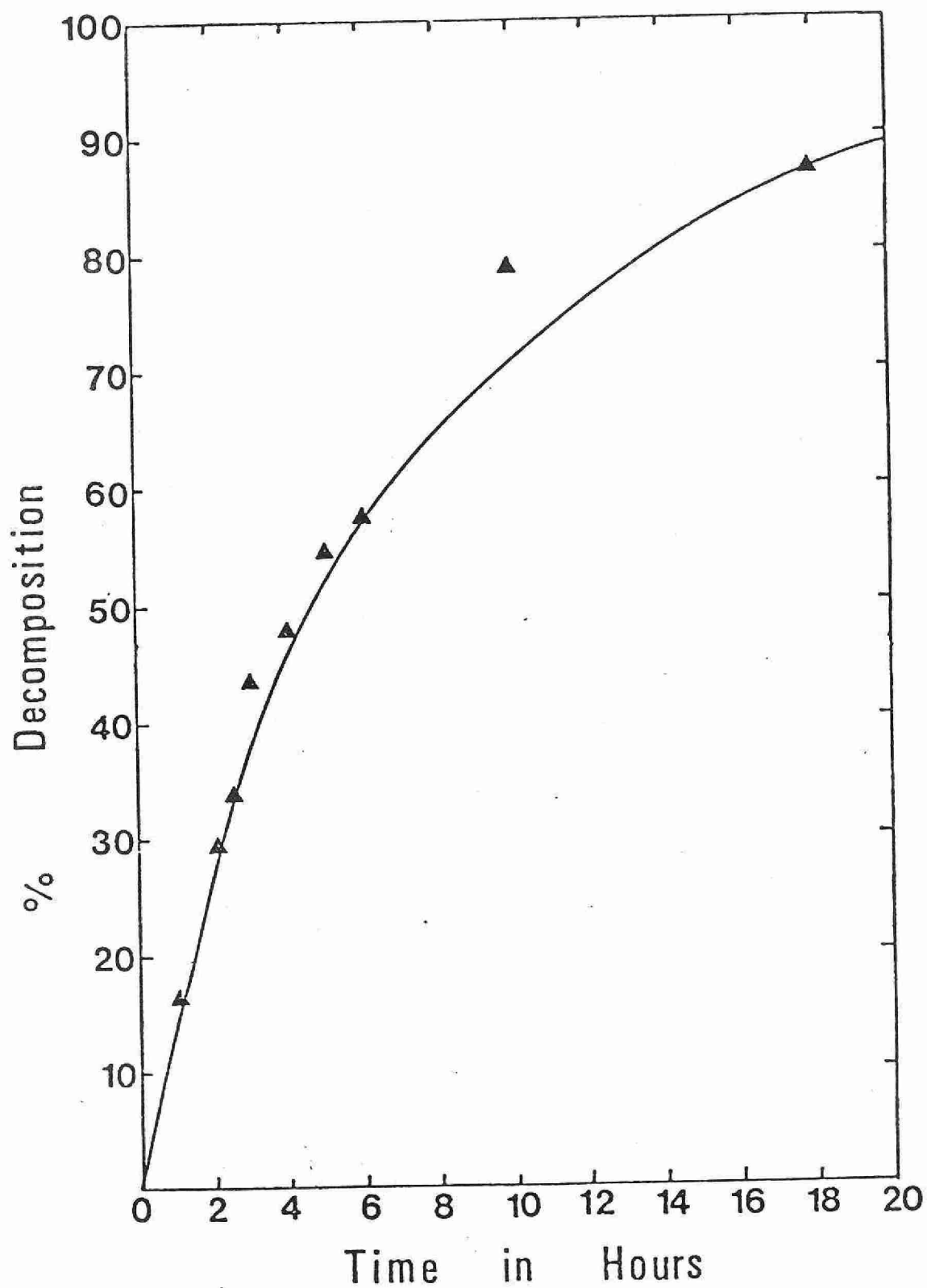


FIGURE 4. THE MODIFICATION OF 1,2,3,4-DIBENZANTHRACENE
UNDER SIMULATED SUNLIGHT IN THE PRESENCE OF
0.2 PPM OF OZONE

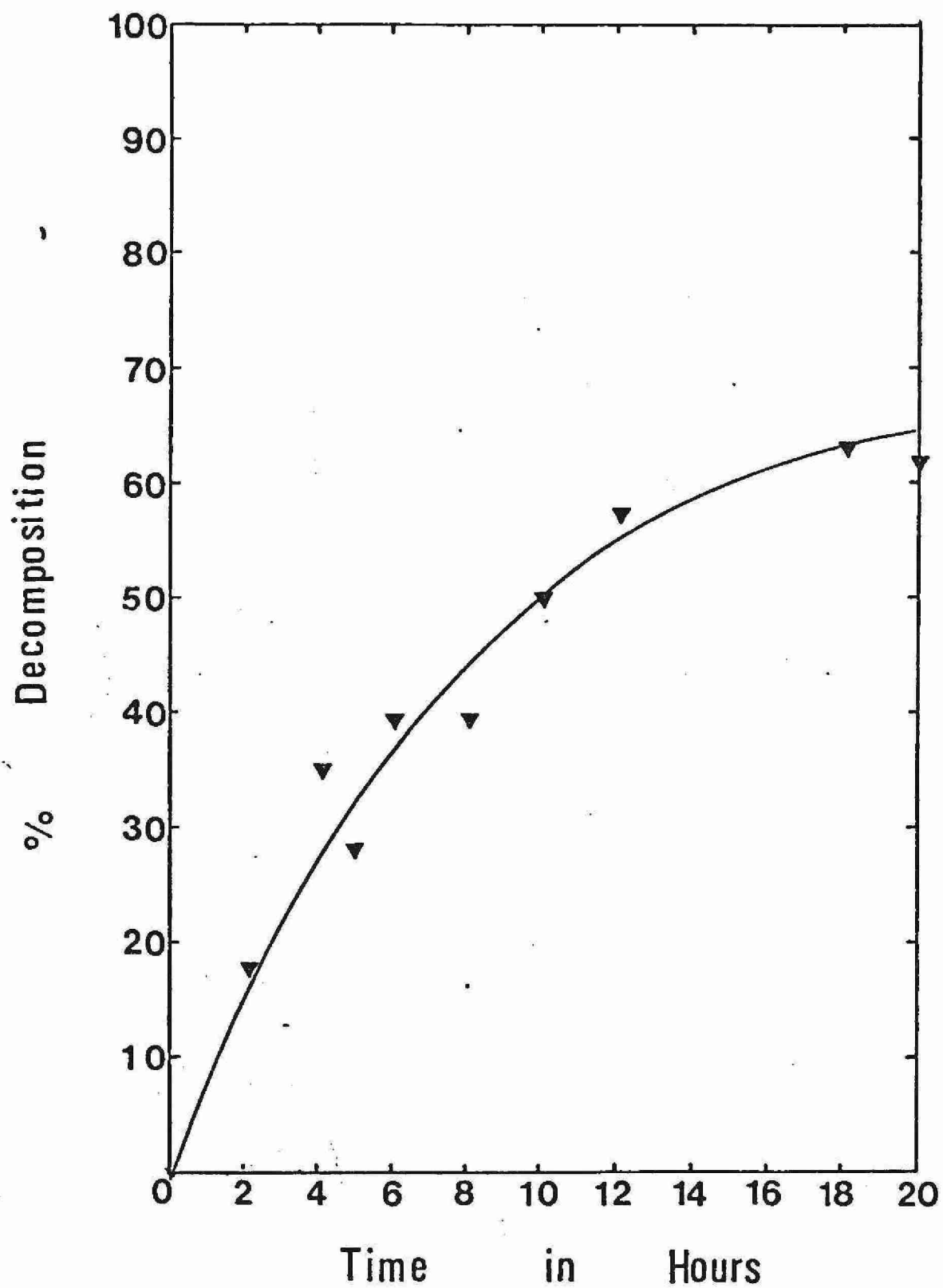


FIGURE 5. THE MODIFICATION OF 1,2,5,6-DIBENZANTHRACENE
UNDER SIMULATED SUNLIGHT

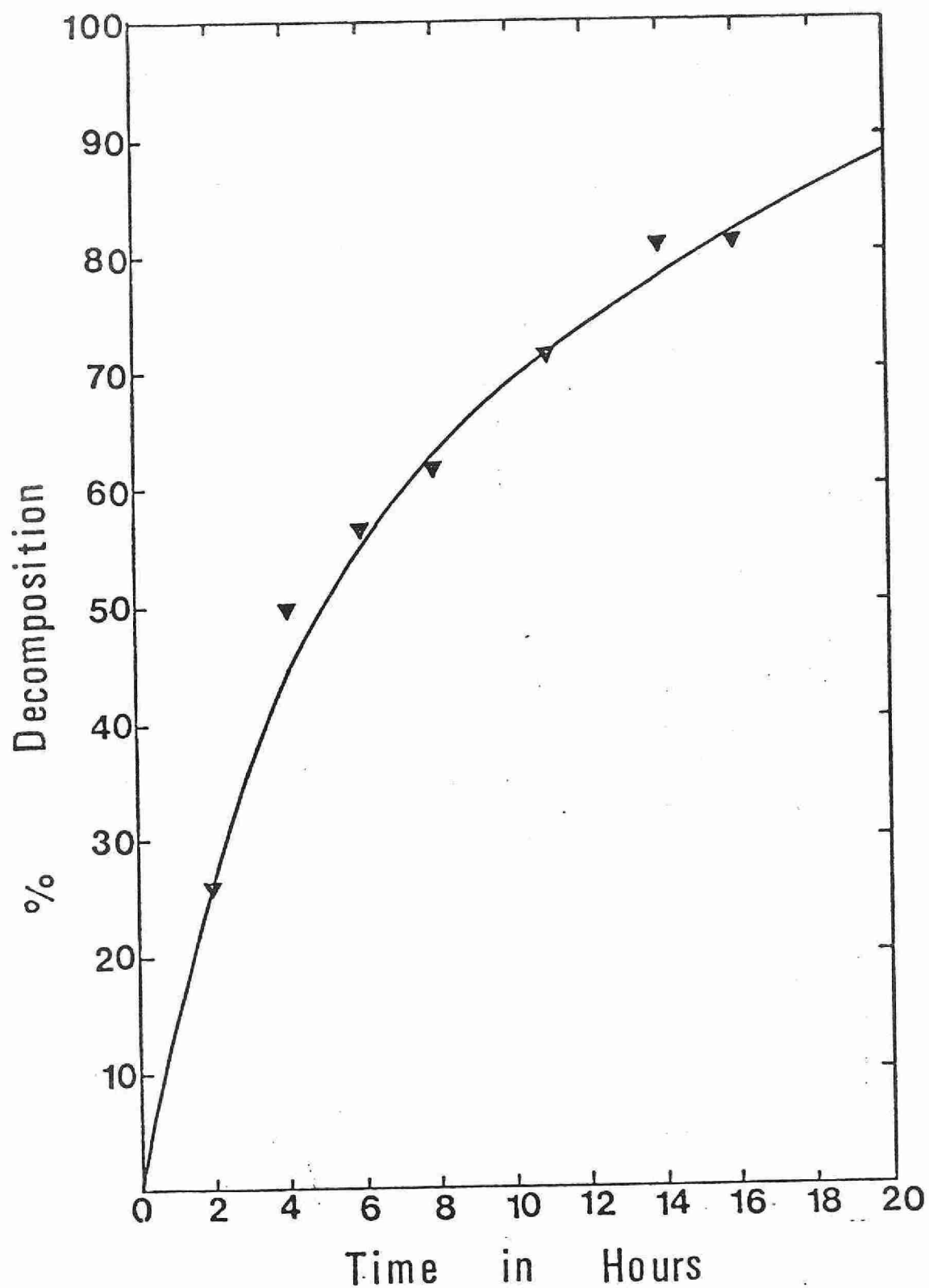


FIGURE 6. THE MODIFICATION OF 1,2,5,6-DIBENZANTHRACENE
UNDER SIMULATED SUNLIGHT IN THE PRESENCE OF
0.2 PPM OF OZONE

A log decomposition versus time plot of 1,2,5,6-dibenzanthracene during oxidation experiments with 0.2 ppm of ozone in the dark is shown in Figure 9.

Similar reaction rate studies of the photodecomposition and oxidation of 1,2-benzanthracene are illustrated graphically in Figure 10. The experimental data conform to that of a first order reaction rate. Similar studies were carried out with 4,5-benzpyrene (benzo(e)pyrene) (BeP) (Figure 11).

A summary of the data on the photodecomposition and oxidation of these PAH compounds is presented in Table 3. The half-lives ($t_{1/2}$) of the above PAH, along with those for benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF) and benzo(k)fluoranthene (BkF), as published by Lane and Katz (32), are presented in Table 4. In this series of PAH, benzo(a)pyrene and 1,2 benzanthracene show the highest photodecomposition and oxidation rates, as indicated by their half-lives. Benzo(e)pyrene exhibits the greatest resistance to photodecomposition and oxidation or the highest $t_{1/2}$ values. The behaviour of the two isomeric dibenzanthracenes is similar, as evidenced by their $t_{1/2}$ values for exposure to irradiation and irradiation in the presence of ozone. These PAH compounds are much more resistant to photodecomposition in simulated sunlight than they are to oxidation by 0.2 ppm ozone in the dark.

The relative carcinogenicity of these PAH compounds is shown in Table 5. There is some evidence that the structure of PAH compounds and their carcinogenic potential are related to reactivity for formation of quinones and epoxides. The large difference in rates of oxidation of the isomers, benzo(a)pyrene and benzo(e)pyrene, and in their carcinogenic activity

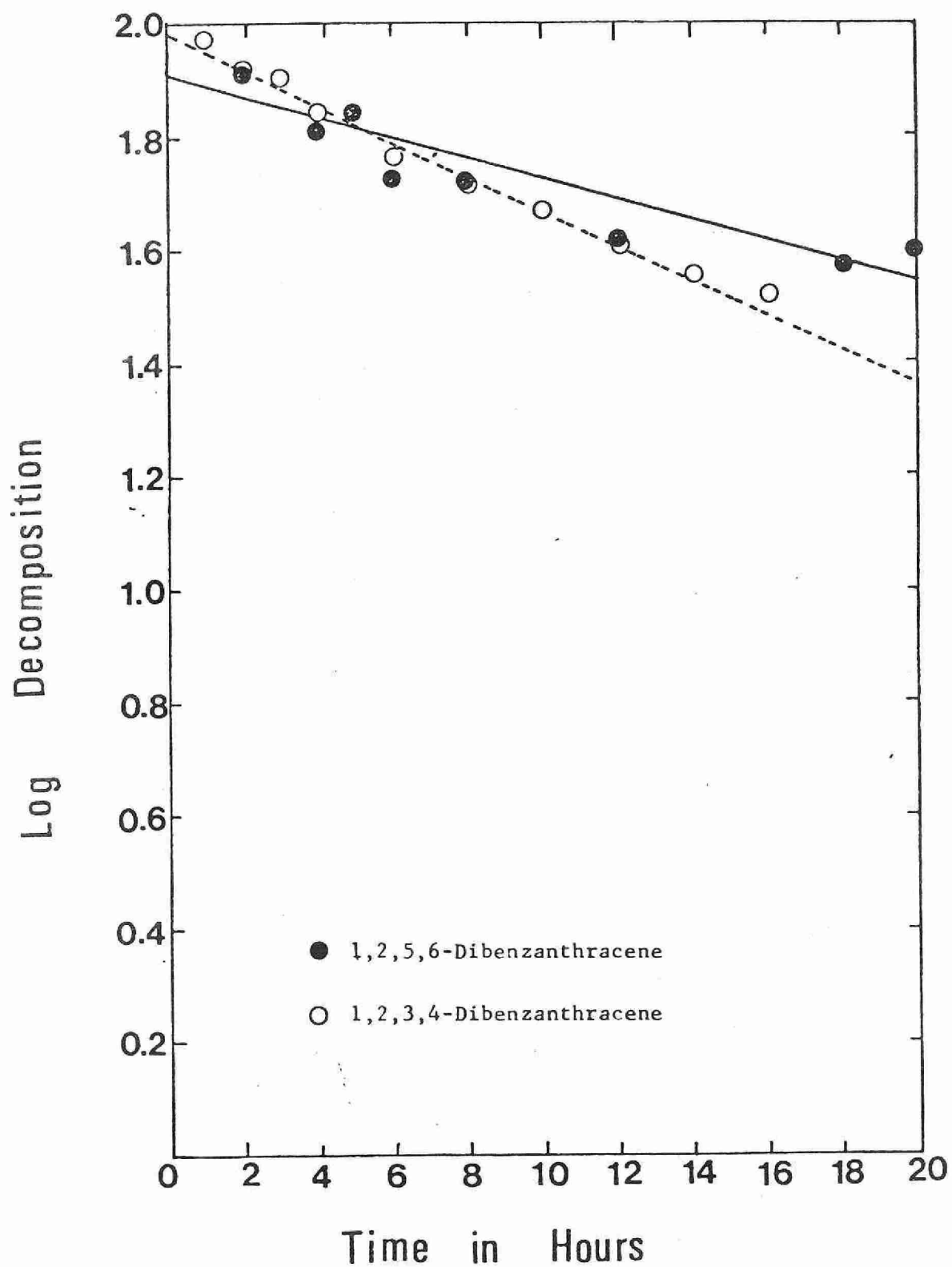


FIGURE 7. DECOMPOSITION OF 1,2,3,4-DIBENZANTHRACENE AND
1,2,5,6-DIBENZANTHRACENE UNDER SIMULATED
SUNLIGHT

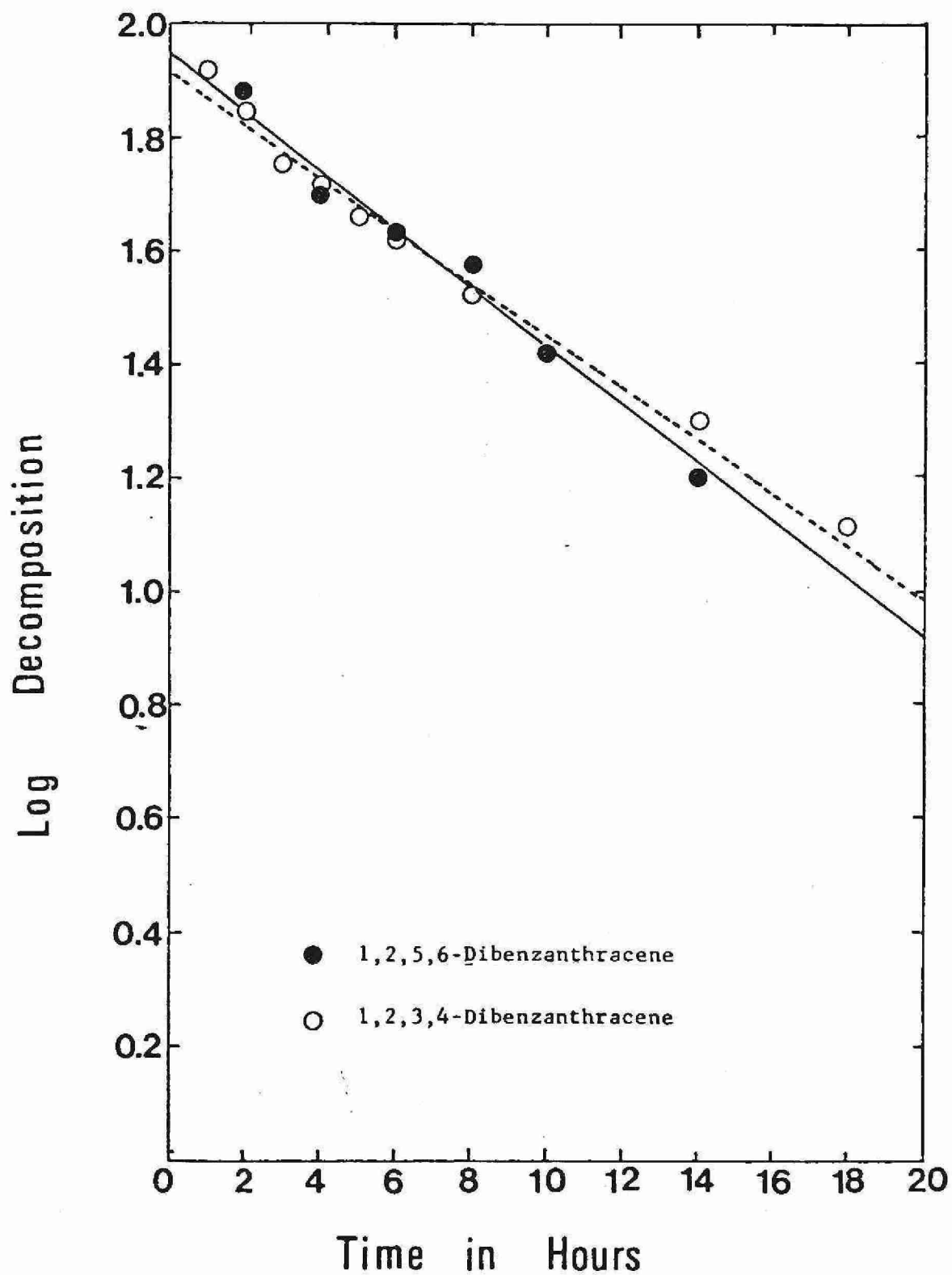


FIGURE 8. DECOMPOSITION OF 1,2,3,4-DIBENZANTHRACENE AND
1,2,5,6-DIBENZANTHRACENE UNDER SIMULATED
SUNLIGHT AND 0.2 PPM OF OZONE

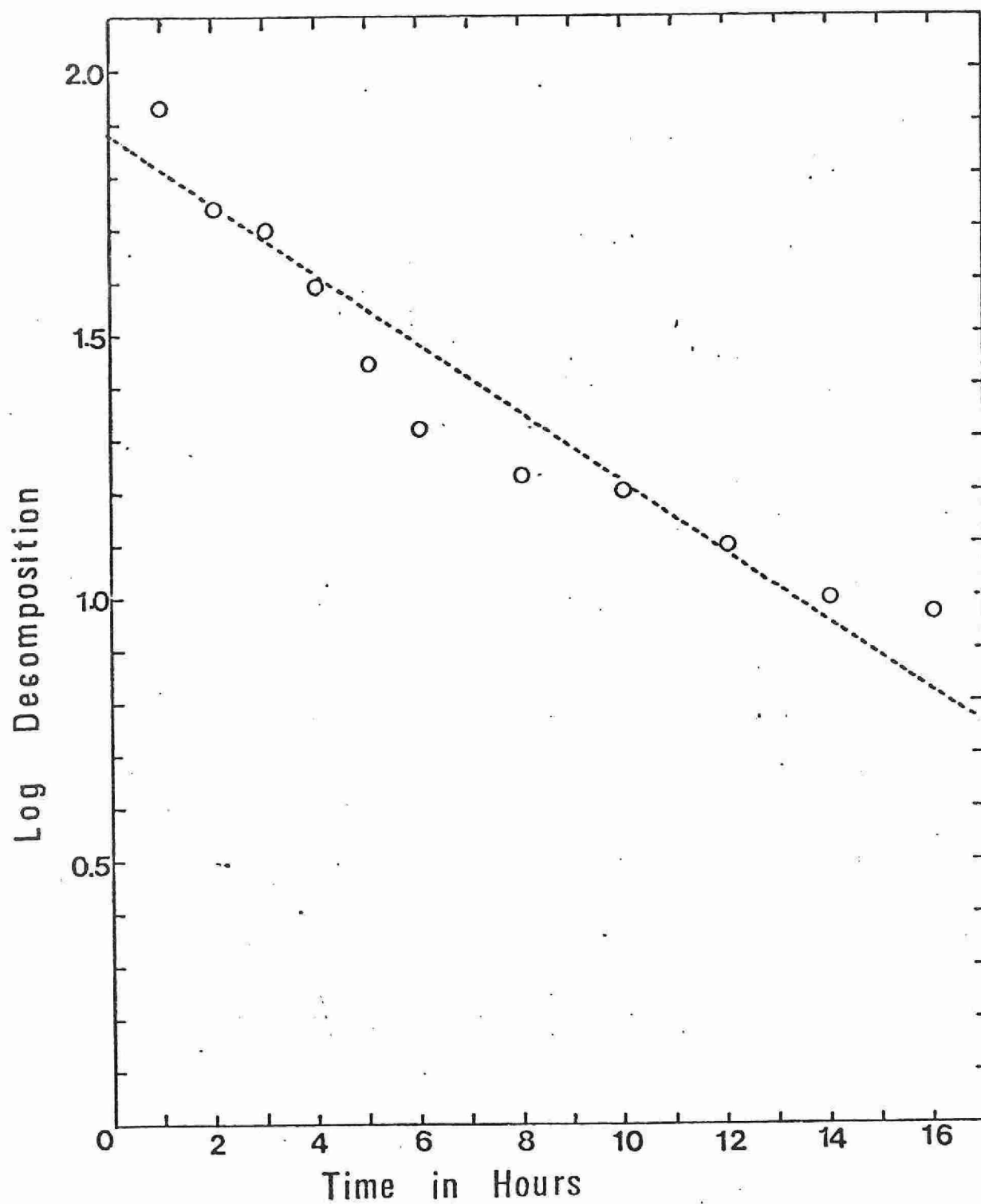


FIGURE 9. THE MODIFICATION OF 1,2,5, 6-DIBENZANTHRACENE UNDER
0.2 PPM OF OZONE IN THE DARK

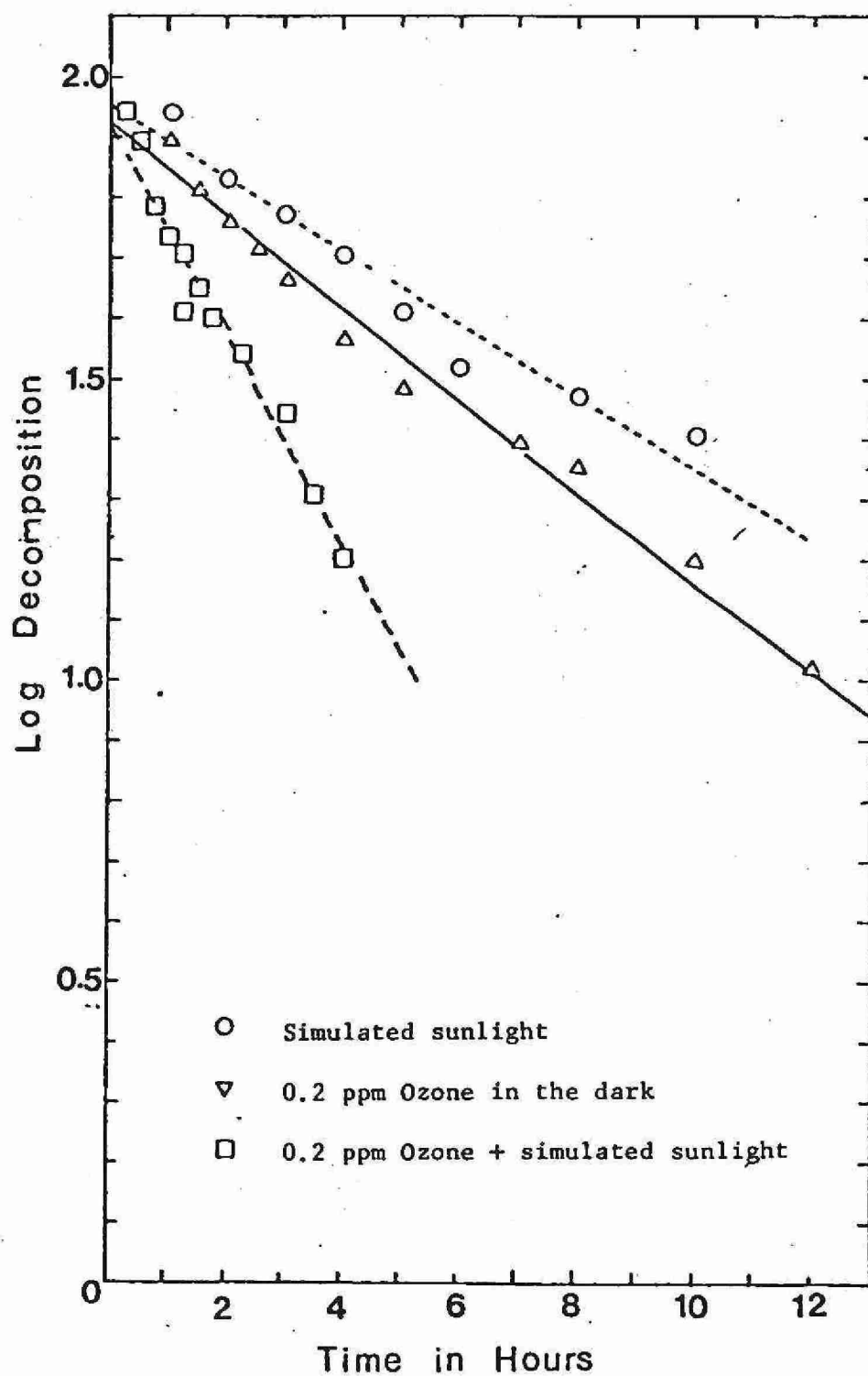


FIGURE 10. THE MODIFICATION OF 1,2 BENZANTHRACENE
UNDER SIMULATED ATMOSPHERIC CONDITIONS

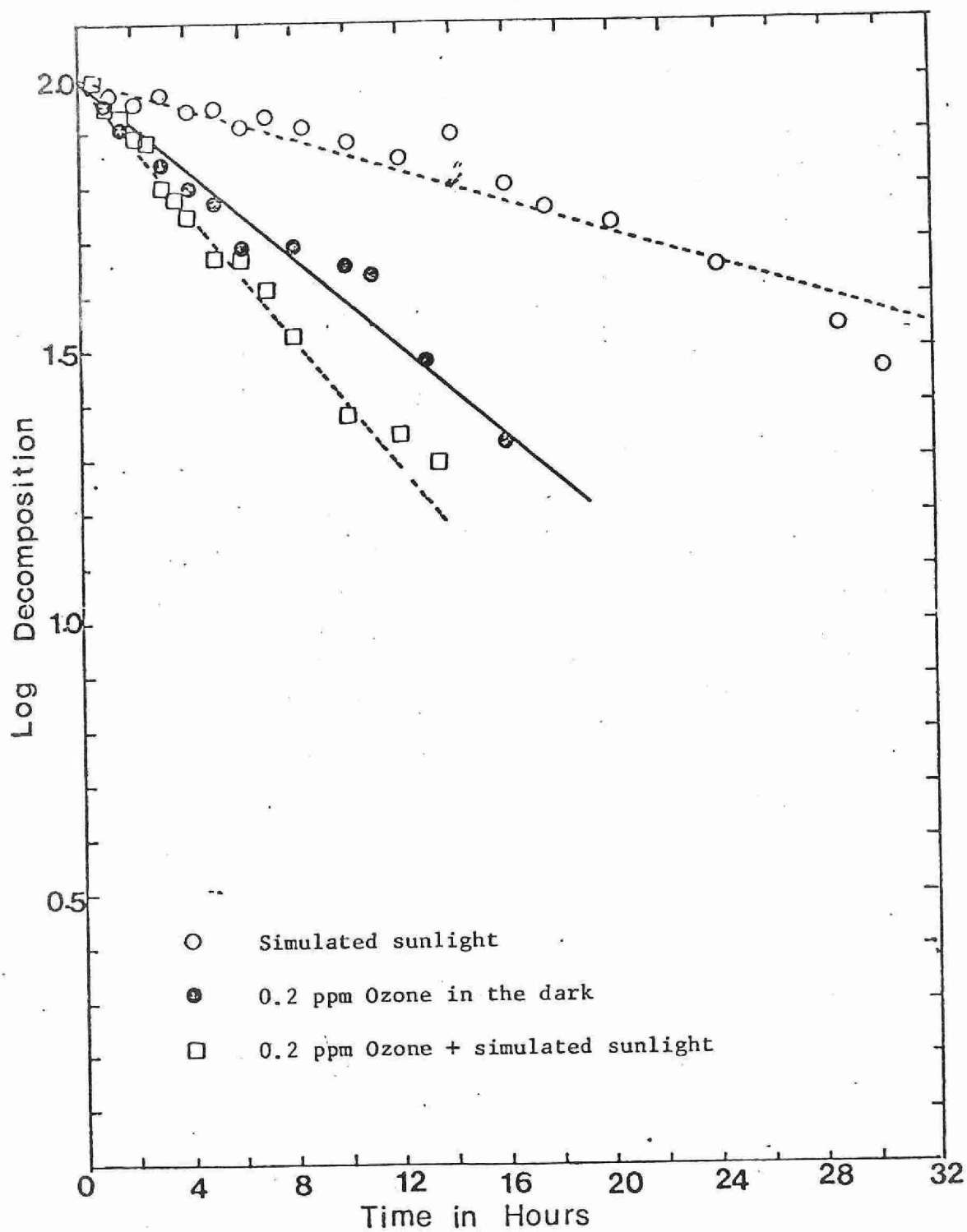


FIGURE 11. THE MODIFICATION OF 4,5-BENZPYRENE UNDER SIMULATED
ATMOSPHERIC CONDITIONS

TABLE 3. Decomposition of Polycyclic Aromatic Hydrocarbons under Simulated Atmospheric Conditions
(Expressed in per cent)

	Simulated Sunlight		Simulated Sunlight + Ozone (0.2 ppm)		Dark Reaction Ozone (0.2 ppm)	
	4 Hrs.	8 Hrs.	4 Hrs.	8 Hrs.	4 Hrs.	8 Hrs.
1,2-Benzanthracene	48.7	70.5	83.1	100	59.3	79.3
4,5-Benzpyrene	12.9	20.6	41.1	64.5	33.9	51.2
1,2,5,6-Dibenzanthracene	30.72	39.9	43.9	60.5	63.7	78.1
1,2,3,4-Dibenzanthracene	29.0	47.5	48.2	62.0	-	-

TABLE 4. Half-lives of Polycyclic Aromatic Hydrocarbons under Simulated Atmospheric Conditions
(Expressed in hours)

	Simulated Sunlight	Simulated Sunlight + Ozone (0.2 ppm)	Dark Reaction Ozone (0.2 ppm)
1,2-Benzanthracene	4.2	1.35	2.88
4,5-Benzpyrene (Benzo(e)pyrene)	21.1	5.38	7.6
1,2,5,6-Dibenzanthracene	9.6	4.8	2.71
1,2,3,4-Dibenzanthracene	9.2	4.6	-
Benzo(a)pyrene	5.3	0.58	0.62
Benzo(b)fluoranthene	8.7	4.2	52.7
Benzo(k)fluoranthene	14.1	3.9	34.9

TABLE 5

<u>Compound</u>	<u>Carcinogenicity</u>
1,2-Benzanthracene (Benz(a)anthracene)	+ (weak)
1,2,5,6-Dibenzanthracene (Dibenz(a,h)anthracene)	+++ (strong)
1,2,3,4-Dibenzanthracene (Dibenz(a,c)anthracene)	+
Benzo(e)pyrene (4,5-Benzpyrene)	- (negative)
Benzo(a)pyrene	+++
Benzo(b)fluoranthene	++ (intermediate)
Benzo(k)fluoranthene	-

furnish an example of the above relationship. Benzo(a)pyrene is a strong carcinogen, whereas benzo(e)pyrene is not. Biological studies in cell cultures have shown that epoxides of some PAH are much more active as carcinogens than their parent hydrocarbons (27,28). The relation between structure, reactivity towards oxidation and carcinogenic potential of PAH and other chemical carcinogens have been reviewed in a recent monograph (38).

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THE PHOTODECOMPOSITION OF BENZO(a)PYRENE (BaP) IN AQUEOUS MEDIA

I DETERMINATION OF BENZO(a)PYRENE DECOMPOSITION RATE

I.1 PREPARATION OF SYNTHETIC SOLUTIONS IN DEIONIZED WATER

Although the presence of BaP in natural waters has been determined, the state of BaP (i.e. whether it is present as a suspension or is truly soluble) has not yet been confirmed. BaP has been forced into an aqueous solution by first dissolving it in either an organic solvent, acetone or benzene, then spiking water with known amounts of this solution (1,2). It has been since found (3), however, that acetone may act as a photosensitizer for condensed PAHs such as BaP, therefore, an acetone/BaP/water solution was not a good system for use in a photosensitized reaction.

An initial attempt to produce an aqueous solution of BaP in deionized water involved simply stirring the water with BaP crystals; but closer observation revealed small crystals which had not dissolved, resulting in a very low concentration of dissolved BaP (i.e. approximately 5 ppb).

The method of producing an aqueous solution of BaP was based on the absence of solvent effects of methanol on BaP photodecomposition. This fact has been confirmed by several investigators (2), and permits BaP to be first dissolved in methanol, then adding deionized water to produce a 50% methanol/water solution of BaP. This method was reproducible in allowing a solution of 1-10 ppm of BaP to be made.

1.2 PREPARATION OF SYNTHETIC SOLUTIONS IN POND WATER

To study sensitized photodecomposition of BaP, natural water samples from a pond were collected. Approximately 20 l. of water containing brown, humic matter was collected from Grenadier Pond in west Toronto. The water was filtered through a 0.5 micron filter, to sterilize, and subsequently stirred for 72 hours with a small amount of crystalline BaP. After stirring, the solution was allowed to settle for 2-4 days, after which aliquots of solution were carefully siphoned off. This method provided reproducible solutions containing 5-10 ppm of BaP, thus hopefully reproducing conditions found in a naturally polluted stream or pond.

1.3 PREPARATION OF FULVIC ACIDS

To increase absorption of light by dissolved organics (specifically fulvic acid) in the pond water, excess fulvic acids were added to the BaP/pond water solutions during irradiation.

The fulvic acid was prepared according to the extraction method outlined by Schnitzer and Khan (4), commonly used to remove fulvic acid from soils.

Approximately one kilogram of soil was collected from the grounds of York University. After stirring the soil with 1 litre of 0.5 N. sodium hydroxide, the pH was adjusted to 2 with hydrochloric acid, and was left undisturbed for 5 days at 2°C. During this time, the solution separated into a dark brown precipitate (humic acids) and a brown

solution, containing the fulvic acids. The brown solution was decanted and filtered through Whatman no. 1 filter paper then evaporated to dryness, under vacuum at 30°C. The remaining brown fulvic acid was used as the photosensitiser during later irradiation of the aqueous BaP.

1.4 REACTION SYSTEM

As sunlight passes through the atmosphere, its intensity is decreased through absorption by atmospheric gases, such as ozone, and by molecular and aerosol scattering. The transmittance of the atmosphere in the ultra-violet and visible region varies in direct relation to wavelength. Essentially no light is transmitted at wavelengths less than 295 nm. The sharp decrease in intensity in the 280-320 nm region is due mainly to ozone absorption. Therefore, the part of sunlight responsible for direct photolysis of many pollutants is the UV radiation above 295 nm.

In order to simulate the spectral distribution of natural sunlight, black light fluorescent lamps, sunlamps and laboratory fluorescent lamps have traditionally been used in past decomposition studies. More recently, however, a General Electric Quartzline Q500T3/CL 500 watt lamp, mounted in a standard photographic housing at a distance of 45 cm above the reaction vessels, has been used (5). For this lamp, Lane compared the spectral intensity distribution of natural sunlight for the zenith angles of 40 degrees (as reported by Leighton) and the spectral output of the lamp, as measured by a spectrophotometer. Lane found the lamp to closely approximate the spectral energy distribution of the sun

for a zenith angle of 50 degrees, in the photochemically important range of 295-400 nm. A 0.3 cm thick Pyrex disc is used to cut off light at 295 nm, otherwise radiation is available down to 240 nm.

Therefore, the General Electric Quartzline lamp was the light source used for the photodecomposition of BaP. In the initial experimentation, it was found, however, with no Pyrex cover on the sample, that the lamp generated heat which led to sample evaporation. Therefore, a copper cooling coil was fitted around the reaction vessel to

eliminate this problem. This cooling coil was used in all experiments, not only to eliminate evaporation but also to avoid any reaction which may occur on an increase in temperature.

The irradiation source, as well as the cooling coil were installed inside a closed box to eliminate effects from laboratory fluorescent illumination.

1.5 IRRADIATION OF BENZO(a)PYRENE WITH ULTRA-VIOLET LIGHT

Two hundred and fifty millilitre aliquots each of the prepared stock solutions of BaP in deionized water and in pond water were stirred and irradiated in the described photoreactor. The samples were exposed to UV radiation of (a) wavelengths of 240-400 nm or (b) wavelengths ranging from 300-400 nm (achieved by covering the solutions with a 0.3 cm thick Pyrex watchglass). In order to determine the rate of decomposition the samples were irradiated for periods of time varying from 15 minutes to 70 hours.

The photodecomposition studies involving fulvic acid as the sensitizer were carried out using the pond water stock solution of BaP. One half a gram of solid fulvic acid was added to each solution; this amount of sensitizer was found to absorb UV radiation at this concentration for the wavelength used. The solutions were stirred under a Pyrex watchglass for periods of time ranging from 15 minutes to 70 hours at wavelengths of 300-400 nm.

As a control experiment, stock solutions of BaP in both de-ionized water and pond water were stirred for 24 and 48 hours in the dark. These samples were extracted and analysed by the same methods as the irradiated samples. As a background blank, one litre each of the water used to prepare the methanol/water stock deionized water as well as the pond water were extracted with several aliquots of chloroform, evaporated to 0.5 ml. and analysed by gas chromatograph under the same conditions used for the BaP samples. No significant concentration of interfering organics were detected. From these experiments, background losses, such as absorption onto glass, or onto other dissolved organics, as in the case of the pond water, and possible background BaP levels could be determined.

In order to determine the oxygen dependence of the photodecomposition of BaP, irradiations of methanol/water and pond water solutions of BaP were conducted in degassed solutions. Irradiation of the solution were done in a closed cell while allowing a stream of nitrogen (35 cc/min) to bubble continuously through the solution. The nitrogen used in the degassed solutions was scrubbed through an ammonium meta vanadate solution prepared as follows: 200 g of ammonium meta vanadate (NH_3VO_3) was dissolved in 25 mls of concentrated HCl. This solution was boiled until the salt had dissolved then made up to a 250 ml volume. Meanwhile, 3-4 drops of mercury and several drops of 1N HCl was added to a few grams of mossy zinc in water. When the zinc had amalgamated, it was drained and placed in a bubbler. The vanadate solution was added to the zinc, and nitrogen was passed through the solution until the solution

turned from green to violet. The nitrogen thus prepared was free of oxygen.

Extraction of these samples were done immediately following irradiation with as little exposure to the air as possible. Analysis of the degassed samples were conducted as for decomposition samples.

1.6 EXTRACTION OF BENZO(a)PYRENE/WATER SAMPLES

Following irradiation, the water samples were quantitatively transferred to 500 ml. separatory funnels and extracted with three one hundred ml. volumes of chloroform. All three chloroform extracts were combined and filtered through five grams of chloroform washed sodium sulphate, into round bottomed flasks. Following evaporation under vacuum to a few mililitres, the combined chloroform extracts were made up to exactly 0.5 mls. and stored in the dark, at 2°C until analysis by gas chromatograph.

1.7 APPLICATION OF THE GAS CHROMATOGRAPH AND FLUORESCENCE SPECTROPHOTOMETER

The reaction rates for all three types of photodecomposition of BaP (without a Pyrex filter ($\lambda = 240-400$ nm), with a Pyrex filter ($\lambda = 300-400$ nm) and the sensitized decomposition ($\lambda = 300-400$ nm)) were observed through the use of a gas chromatograph. The chromatograph used was the Varian Aerograph Model 1740 equipped with a flame ionization detector and a linear temperature programmer. The output was recorded on a Varian Model 20 strip chart recorder.

A glass column, 2 mm ID x 4 m, had been packed with 0.75% OV 17 on acid washed Chromosorb W and approximately conditioned at 295°C for several days. Although some bleeding occurred at the higher temperatures during temperature programming, it was not significant enough to interfere with the BaP elution.

The nitrogen (Matheson prepurified), hydrogen (Matheson Ultra High Purity) and air (Matheson Zero Gas) used were purified by use of inline filters.

The flow rates, operating temperatures and the temperature programming rate used during the gas chromatographic analysis are listed in Table 1.

A better understanding of the mechanism involved in the decomposition of BaP in both deionized and pond water was provided by fluorescence spectra of BaP run in the presence and absence of oxygen on the Perkin Elmer MPF-2A Fluorescence Spectrophotometer. BaP dissolved in methanol/water was excited at 254 nm and 368 nm and the emission was recorded from 400-500 on a Hitachi Recorder.

2. DEVELOPMENT OF THE CAPILLARY COLUMN

Developing an efficient capillary column is more complex than producing a good packed gas chromatographic column. Not only does the type of stationary phase have to be considered (as for packed columns) but the condition of the inner capillary wall as well as the types of the column material have to be determined. Therefore, the preparation of the

TABLE 1
Gas Chromatographic Conditions for
Packed Column

Type of Packing	0.75% OV 17 on acid washed Chromosorb W
Column Dimensions	2 mm ID x 4 m
Carrier Gas:	nitrogen
flow:	30 ml/min
Flame Gases:	hydrogen
flow:	25 ml/min
	air
flow:	250 ml/min
Injector Temperature	290°C
Detector Temperature	220°C
Column Temperature	180°C-295°C (4°C/min)

capillary column is a two-step procedure involving: (i) the type of column material used and its method of etching and deactivation; (ii) the type of stationary phase used to coat the column material.

2.1 TYPE OF COLUMN MATERIAL AND THE METHOD OF PREPARATION

The inertness of glass as a column material outweighs the advantage of the ease of handling of any metal columns, therefore, thick-walled, soft, flint glass tubing (7 mm OD, 2 mm ID) was used to prepare the capillary tubing.

Before drawing, it was necessary to clean the interior walls of the tubing with concentrated hydrochloric acid, ammonium hydroxide, carbon tetrachloride, water and acetone, and to dry thoroughly with a stream of dry nitrogen (to prevent any carbonization on the inside walls during the drawing procedure). The glass tubing was drawn using the Shimadzu GDM-1 glass drawing machine.

The clean, thick-walled glass tubing is driven by the feeding rollers through the oven (temperature = 440°C) and passed through the heated (320°C) stainless steel coiling tube. By changing the ratio of the feeding rollers and the drawing rollers the interior diameter can be varied. The capillary inner diameter is calculated from the equation:

$$D_2 = D_1 / \sqrt{W}$$

where D_2 is the inner diameter of the capillary column, D_1 , the inner diameter of the thick-walled tubing and W is the drawing ratio. For ex-

ample, thick-walled tubing (7 mm OD, 2 mm ID, 1.5 m length) drawn at a ratio of 64:

$$D_2 = \sqrt{\frac{1}{64}} (2 \times 10^{-1}) \text{ cm} \\ = 0.25 \text{ mm}$$

produces a coiled capillary with 0.7 mm OD, 0.25 mm ID, length of approximately 96 m.

2.2 : ETCHING METHOD

After drawing, it was necessary to increase the critical surface tension of the inner capillary wall by surface roughening to insure the development of a smooth film of stationary phase, rather than the accumulation of tiny droplets. Several methods of surface roughening were evaluated, but because of successful results achieved in this area by Onuska and Comba (6), it was decided to etch the capillary column with gaseous hydrogen fluoride.

Two methods of using hydrogen fluoride (HF) as the etching gas were tried: (a) direct application of the HF gas and (b) HF gas produced from the heating of ammonium hydrogen difluoride salt.

Under the first method, a closed stainless steel system was made, since the safety precaution is a main consideration when using HF gas. During experimentation, it was found that the capillary tube nearest to the HF source, became quickly clogged with silica because of the extreme corrosive nature of the gas. Therefore, the system was altered so that a small portion of nitrogen could be mixed with the HF. The

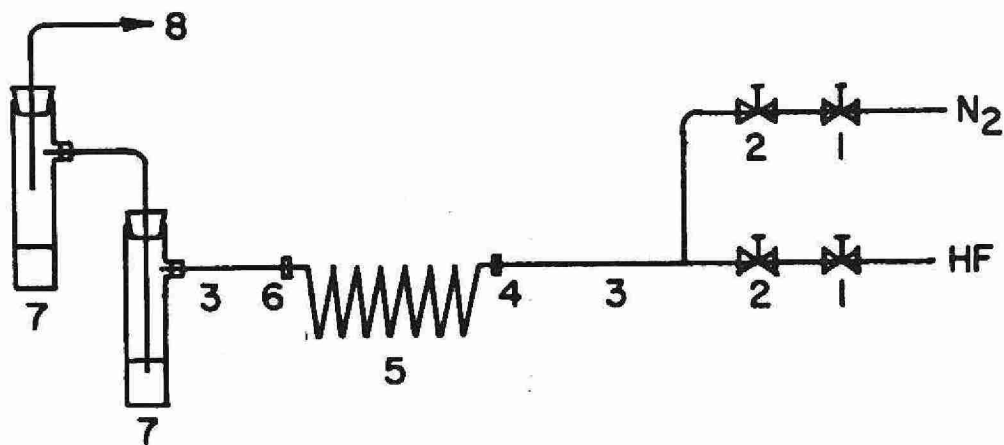
nitrogen-HF mixture insured passage of the gas through the column in the flow system illustrated in Figure 1.

After allowing the HF to pass through the column, valve 1 was closed and the column was sealed off, using a microflame torch. The sealed column was heated from ambient temperature to 400°C for 12 hours and then cooled and flushed in a fume hood with nitrogen for two hours. The column now had an opaque appearance.

The second method of etching used was developed by Onuska et al (7) during the experimentation for this thesis. This new method was based on indirect etching by HF. The HF gas was produced from heating ammonium hydrogen difluoride salt trapped within the column. This method has two advantages over the direct application of HF gas onto glass: (a) it is by far safer to use the salt than be exposed to the noxious gas and (b) in a very short time, the extreme corrosive nature of the HF gas had pitted and clogged several of the stainless steel connections of the nitrogen/HF flow system.

Therefore, although etching by direct exposure to HF is an adequate method for surface roughening, it was decided to use indirect etching by HF produced from ammonium hydrogen difluoride salt.

The procedure for using ammonium hydrogen difluoride salt is as follows: the freshly drawn capillary columns were filled with concentrated HCl, sealed and heated overnight at 80°C. After cooling, the acid was removed and the column washed with distilled water, acetone, diethyl ether and dried with a stream of nitrogen. The column was



- | | |
|--------------------------|--------------------------|
| 1 toggle valve | 5 capillary column |
| 2 metering valve | 6 capillary - 1/4" union |
| 3 stainless steel tubing | 7 ammonia trap |
| 4 1/4" - capillary union | 8 vacuum |

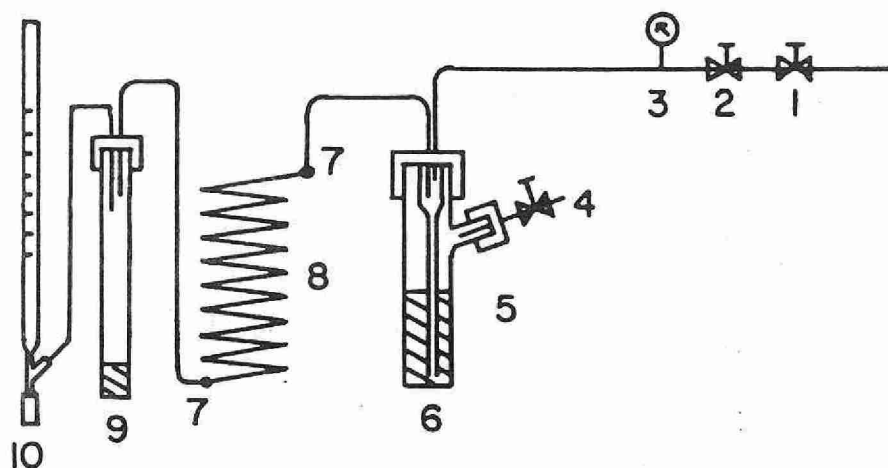
FIGURE 1 . Gaseous HF/N₂ etching system

filled with a 2.5% (W/V) saturated solution of ammonium hydrogen difluoride in methanol, and allowed to stand for one hour. The methanol was then removed by a uniform nitrogen flow until the column appeared milky. The column ends were sealed and the column was placed into a muffle furnace at 450°C for three hours. After cooling, the column was washed with methanol and blown dry with nitrogen.

2.3 DEACTIVATION OF COLUMNS

Blomberg (8) found that silanization after HF etching reduced column activity only slightly towards polar compounds. A well-deactivated surface can be achieved by the method developed by Aue et al. (9) in which the glass surface was deactivated by application of a thin film of Carboway 20M (5-10% W/V). A modification of this method (10) is to dynamically coat the glass twice using a solution of Carbowax 20M in concentrations of less than one percent. The lower concentration of the Carbowax was used to simply mask the active silica sites rather than deposit a film on the inner wall. Grob (10) had found the higher concentration (i.e. greater than one percent) not to spread as well as the more dilute solutions.

Therefore, the deactivation treatment as described by Grob, was used as follows: a solution of 1% Carbowax 20M in methylene chloride was passed through a freshly etched capillary column at a normal coating rate of 0.5 to 1 cm per second. The column was dried by a stream of nitrogen then mounted in a gas chromatograph with the detector end free. Keeping the chromatograph at room temperature, the column was flushed



- | | |
|------------------------------|------------------------------|
| 1 toggle valve | 6 coating tank |
| 2 metering valve | 7 column connector |
| 3 pressure regulator | 8 glass capillary column |
| 4 inlet for coating solution | 9 coating solution collector |
| 5 coating solution | 10 flow meter |

FIGURE 2. **Shimadzu Micro-Column Treating Stand**

Source : Shimadzu MCT - IA Instruction Manual

consequently pushed the stationary phase through the column. The nitrogen pressure was adjusted such that the flow of film through the column was 5 cm/sec.

After passing through the column, excess liquid collected in the collector (8), and nitrogen was blown through the column overnight.

Before use, approximately one meter was removed from each end of the column to insure consistency of coating over the entire length of column to be used in the analysis, resulting in a capillary column 10 meters in length.

3. CAPILLARY CHROMATOGRAPHIC SYSTEM

A Shimadzu Mini-GC, constructed especially for capillary columns, equipped with a flame ionization detector and linear temperature programming, was used for all analysis requiring capillary chromatography.

With one exception, the design of the Shimadzu capillary gas chromatograph was similar to chromatographs using packed columns. Samples can be introduced onto packed columns using the conventional 5 or 10 μ l syringe. Unfortunately, since the capillary columns have a very limited sample capacity (10^{-2} to 10^{-3} μ l) which can be introduced without overloading the column, samples cannot be introduced with the usual syringe. The smallest syringe has a capacity of 0.5 μ l but volumes less than 0.1 μ l cannot be introduced reproducibly.

To overcome this difficulty, an indirect sampling procedure may be used: a large amount of sample (0.5 to 2.0 μ l) is injected into the

system but, following solvent evaporation and uptake of the sample by nitrogen, the sample is split into two unequal parts. The smaller part of the sample enters the capillary column, the larger is discarded. In this way, the actual sample entering the column will be a fraction of the original.

The split ratio for samples analysed on the Shimadzu Mini-GC was 20:1 (i.e. 20 parts discarded while 1 part entered the column).

4. PREPARATION OF STANDARD SOLUTIONS

4.1 QUINONES

Oxidation of adsorbed BaP, in the presence of UV light and ozone, has been found to result in a mixture of the three BaP quinones - 6,12-, 1,6-, and 3,6- BaP diones -- and other minor oxygenated products, far quicker than oxygenation in solution. Rather than individually synthesize the quinones, this principle was used to prepare a mixture of the three diones.

A solution of 200 µg/µl of BaP in chloroform was allowed to coat thin layer plates of silica gel-G. The resulting plates were air dried and oxidized by exposure to UV light for 2-3 hours with a constant stream of ozone (1 ppm). The silica gel was then scraped from the plates onto a filter paper and the irradiation products were then eluted with chloroform. The solutions from several plates were then collected and evaporated to a small amount (approximately 0.1 ml).

To remove other oxidation products as well as unoxidized BaP

from the mixture, the chloroform solution, containing the oxidation products, was percolated through a precleaned micro column of activated silica, until the resulting solution showed no fluorescence due to BaP.

Keefer (11) had reported the use of magnesium hydroxide (Mg(OH)_2) TLC plates to resolve mixtures of quinones, therefore Mg(OH)_2 plates were prepared according to the method outlined by Pierce (12).

The plates were streaked with 3-4 mg of the purified, oxidized chloroform mixture and developed in chloroform. Three distinct bands separated on the TLC plates and could be confirmed as being 6,12-, 1,6-, and 3,6- BaP diones by comparison to R_f values of previous standard solutions.

Each band was removed from the plate, eluted with chloroform and evaporated to form a crystalline compound. Recrystallization was performed on the quinone until a distinct melting point was reached. Solid probe mass spectrometry also confirmed the purity.

The 4,5 dione was synthesized as follows: initially the BaP dihydrodiol was formed from the decomposition of the osmium tetroxide adduct of BaP (13). The dihydrodiol was reacted with a mixture of chromate and pyridine to form the solid orange crystalline 4,5- BaP dione (14). The crude product was recrystallized three times from xylene to obtain a crystalline compound which melted at 258-260°C.

Each of the purified quinones (0.4 mg) were dissolved separately in chloroform (1 ml) and stored in the dark at 2°C. The BaP standard (Aldrich Chemical Co.) was made up similarly.

RESULTS AND DISCUSSION

5. PHOTODECOMPOSITION OF BENZO(a)PYRENE

To determine background losses due to any mechanical or chemical processes, several aliquots of BaP stock solutions in deionized water/methanol and in pond water, were stirred in the reactor for 24 and 48 hour periods in the absence of any illumination. The observed losses are graphically presented in Figure 3.

The deviation of the points from the best straight line fit was $\pm 0.75\%$ or $\pm 0.07 \mu\text{g}$ for deionized water/methanol and $\pm 1.1\%$ or $\pm 0.02 \mu\text{g}$ for pond water. In other similar control experiments, Lane (5) observed a loss of $\pm 3\%$ for a starting solution of 245 ng of BaP and Falk (15), using concentrations of 3-10 μg of BaP observed no loss at all over 48 hours of irradiation.

The above deviations of $\pm 0.75\%$ for BaP in deionized water and $\pm 1.1\%$ in pond water account for BaP losses resulting from BaP transfers between reaction vessels, from BaP recovery from the solutions and from errors in instrumental irreproducibility. Such losses are generally acknowledged as experimental and instrumental errors.

The rest of this section discusses the results obtained from exposing, to an irradiation source simulating sunlight, solutions of: (a) BaP in deionized water/methanol, (b) BaP in pond water and (c) BaP in pond water containing excess fulvic acid. The photodecomposition rates of BaP in these solutions are compared. Based on these decomposition

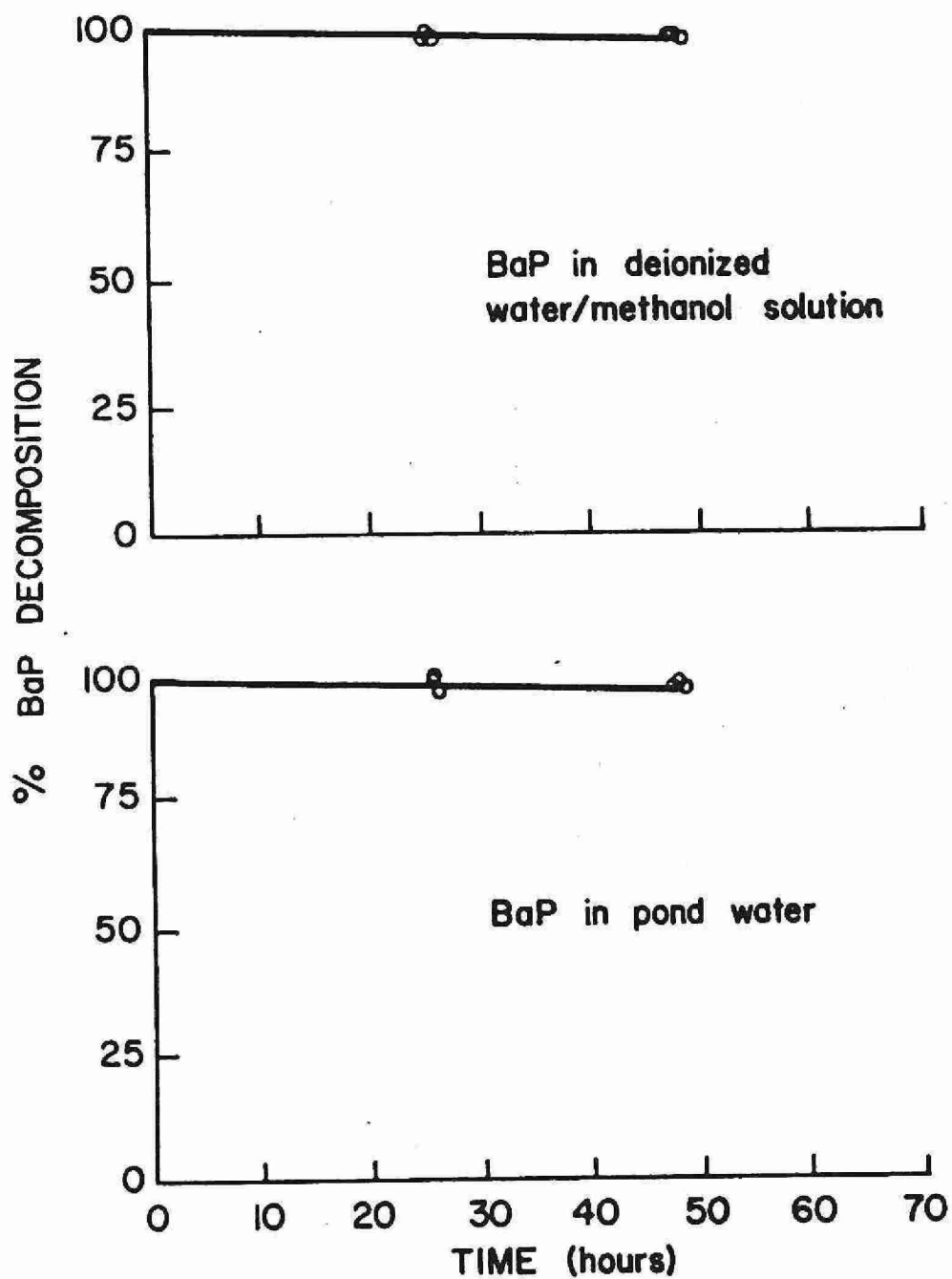


FIGURE 3. Control experiments for dissolved BaP (no irradiation)

rates and on other experimental evidence, mechanisms for these reactions are suggested.

5.1 PHOTOLYSIS OF BENZO(a)PYRENE IN DEIONIZED WATER/METHANOL

Dissolved BaP in methanol/water was irradiated at wavelengths ranging from 240 to 400 nm for varying lengths of time up to 70 hours. Irradiated BaP/methanol/water aliquots were extracted with chloroform and concentrated to small volumes. These samples were then analysed quantitatively using the packed OV 17 gas chromatographic column. The column produced a good chromatograph for BaP elution, as illustrated in Figure 4.

The decreasing levels of BaP in the irradiated samples were plotted over the 70 hour period (Figure 5). It can be seen from the graph that during the first 45 hours of irradiation there is a slow decomposition rate. After this time, decomposition apparently remains constant at 14% BaP decomposition. Plotting the log of BaP concentration over time results in a first order rate of decay for which the rate constant (k) is 0.002/hr.

When a similar series of irradiations were performed under an atmosphere of nitrogen, no decomposition of BaP was found to occur, indicating that oxygen is necessary for decomposition.

By imposing a lower wavelength cutoff at 300 nm, thus allowing light of wavelengths 300 to 400 nm only to affect the solution, little

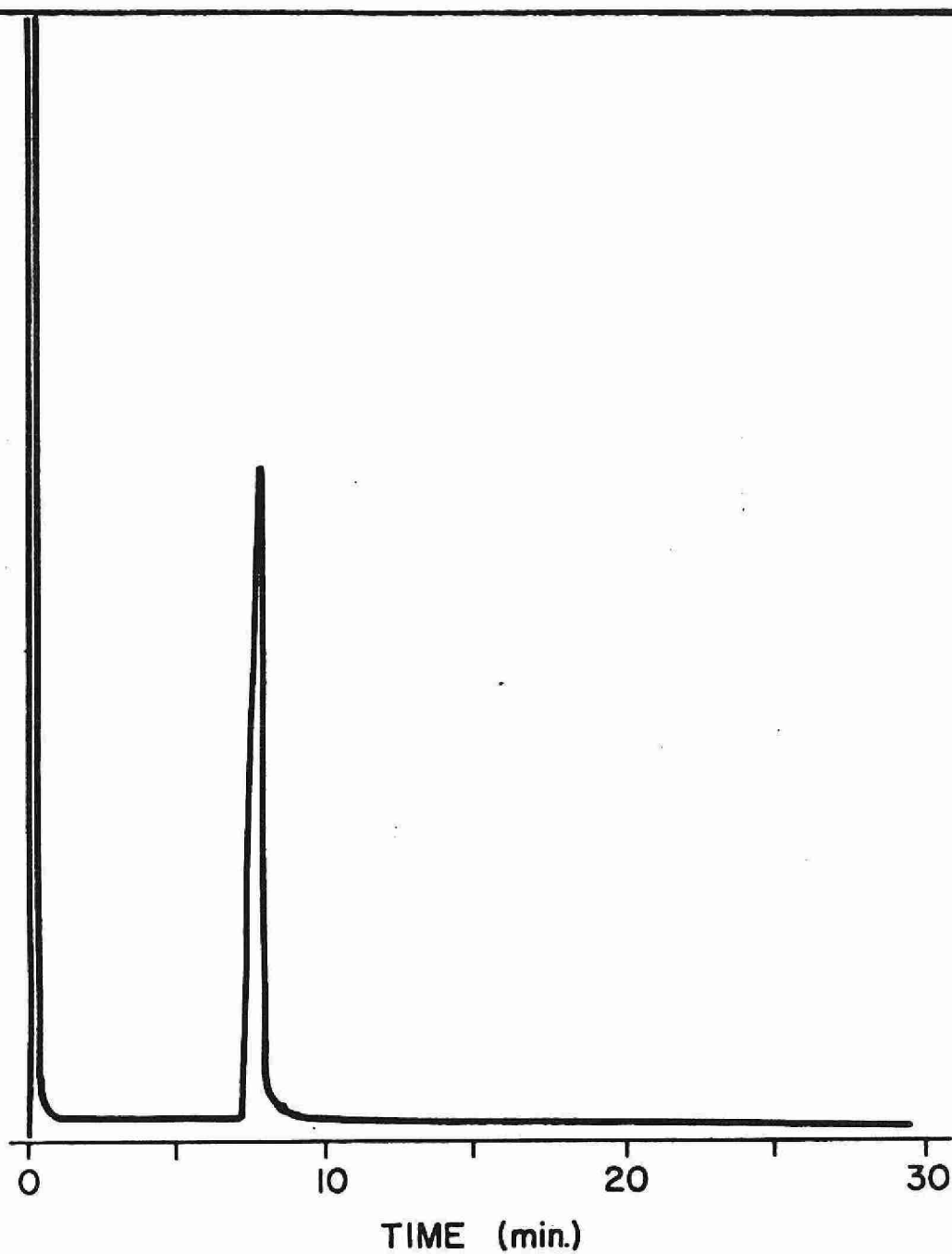


FIGURE 4. Gas chromatogram of BaP standard

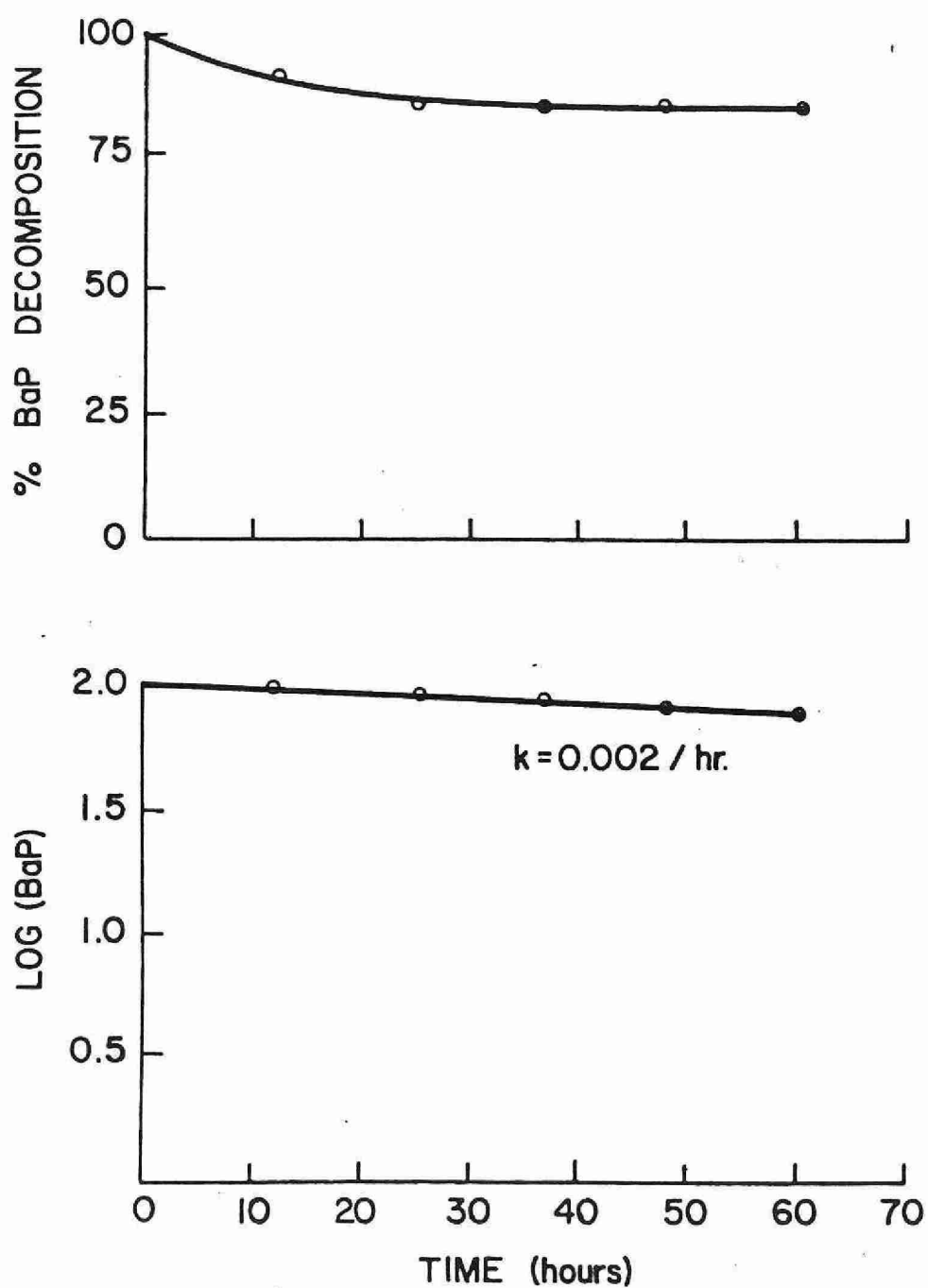


FIGURE 5. Photodecomposition of BaP in deionized water/methanol solution ($\lambda = 240$ to 400 nm)

decomposition of BaP occurred (Figure 6). In fact, the percentage of BaP decomposed fell within the error limits set earlier for deionized water (i.e. ± 0.75). As such, decomposition of BaP in methanol/water under light of wavelengths 300 to 400 nm can be considered negligible.

Emission spectra from BaP excited at 368 nm and 254 nm were observed from 400 to 500 nm. Excitation of BaP at 368 nm produced two broad emission peaks at 406 and 430 nm (Figure 7). The presence or absence of oxygen had no effect on either the position or intensity of the emission.

A similar emission spectrum was observed (i.e. emissions at 406 and 430 nm) from BaP excitation at 254 nm. However, the presence of oxygen was found to quench the emission by 90% (Figure 8).

5.2 PHOTOLYSIS OF BENZO(a)PYRENE IN POND WATER

Irradiations of BaP dissolved in pond water, under light of wavelengths 300 to 400 nm, resulted in a decomposition of BaP. The photodecomposition rate of BaP in pond water is shown graphically in Figure 9, as the percentage of BaP decomposed over time and the log of BaP concentration over time. From the latter graph, the rate constant for decomposition of BaP in pond water was calculated as being $k = 0.004/\text{hr}$.

In the presence of added fulvic acid, the decomposition of BaP in pond water (Figure 10) increased to $k = 0.016/\text{hr}$. No reaction was found to occur for either pond water/BaP solutions or pond water/BaP

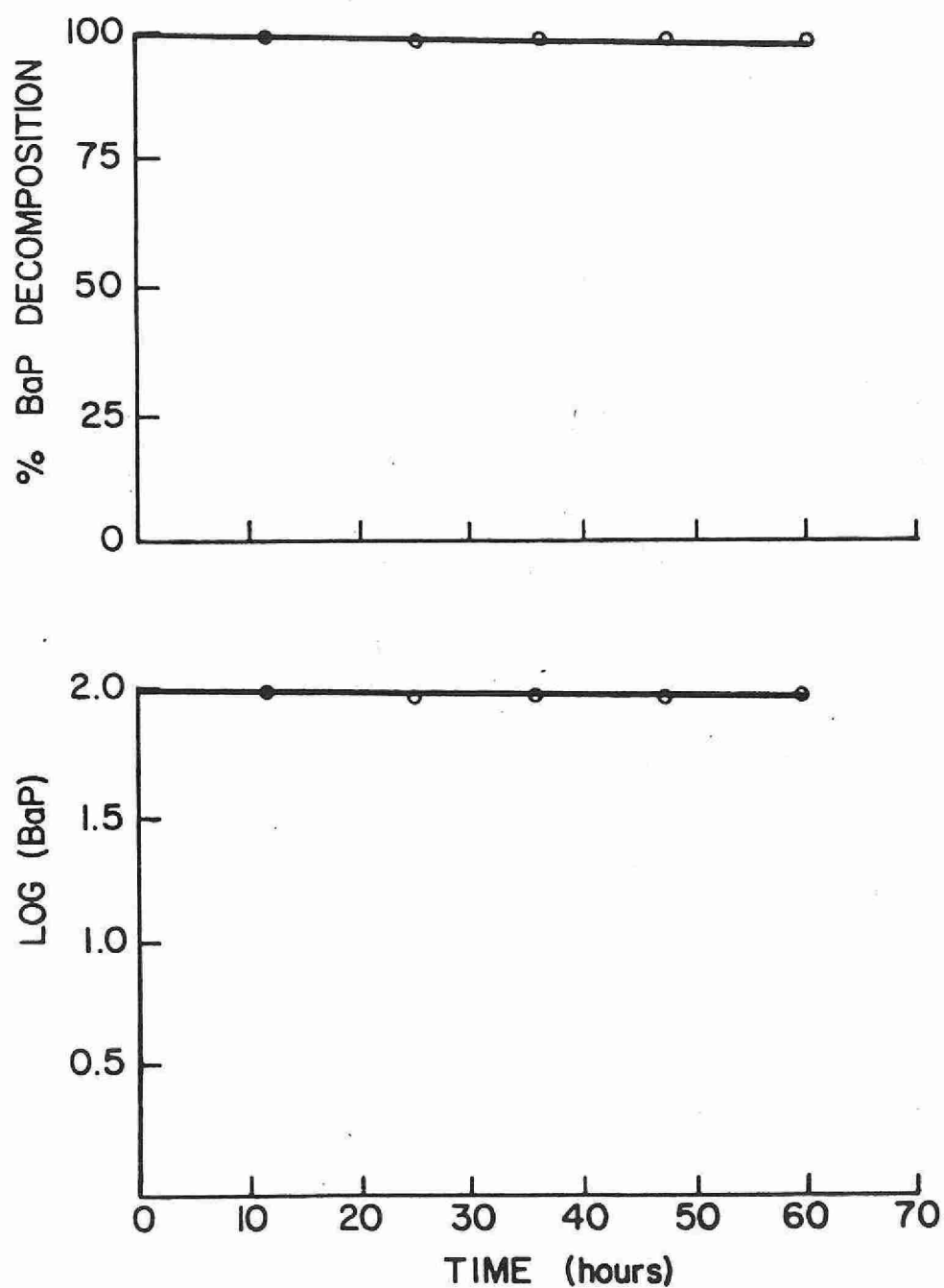


FIGURE 6. Photodecomposition of BaP in deionized water/methanol solution ($\lambda = 300$ to 400 nm)

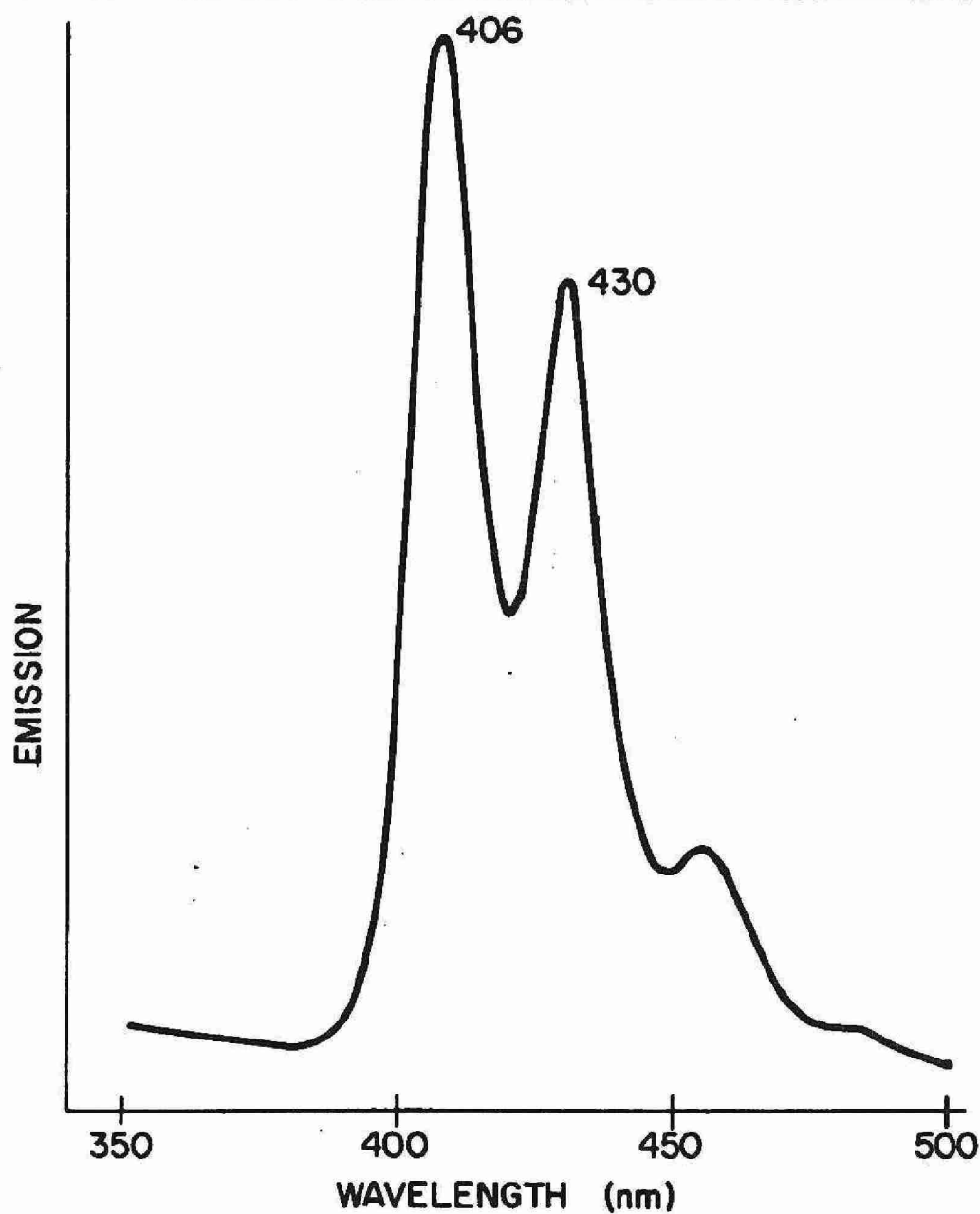


FIGURE 7 . Fluorescence spectrum of BaP in water/methanol solution under air (ex = 368 nm)

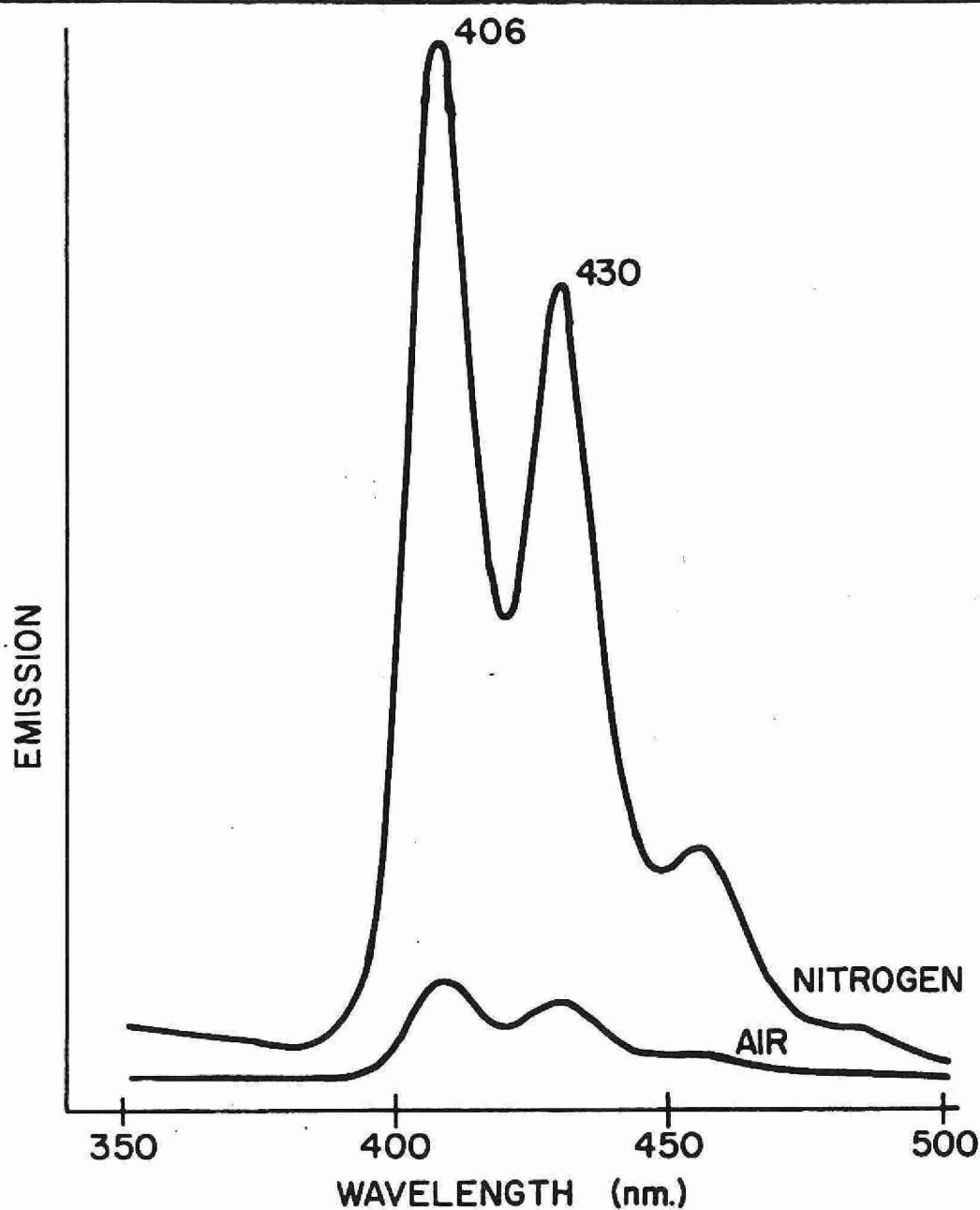


FIGURE 8. Fluorescence spectra of BaP in water/methanol solutions under air and nitrogen (ex = 254 nm)

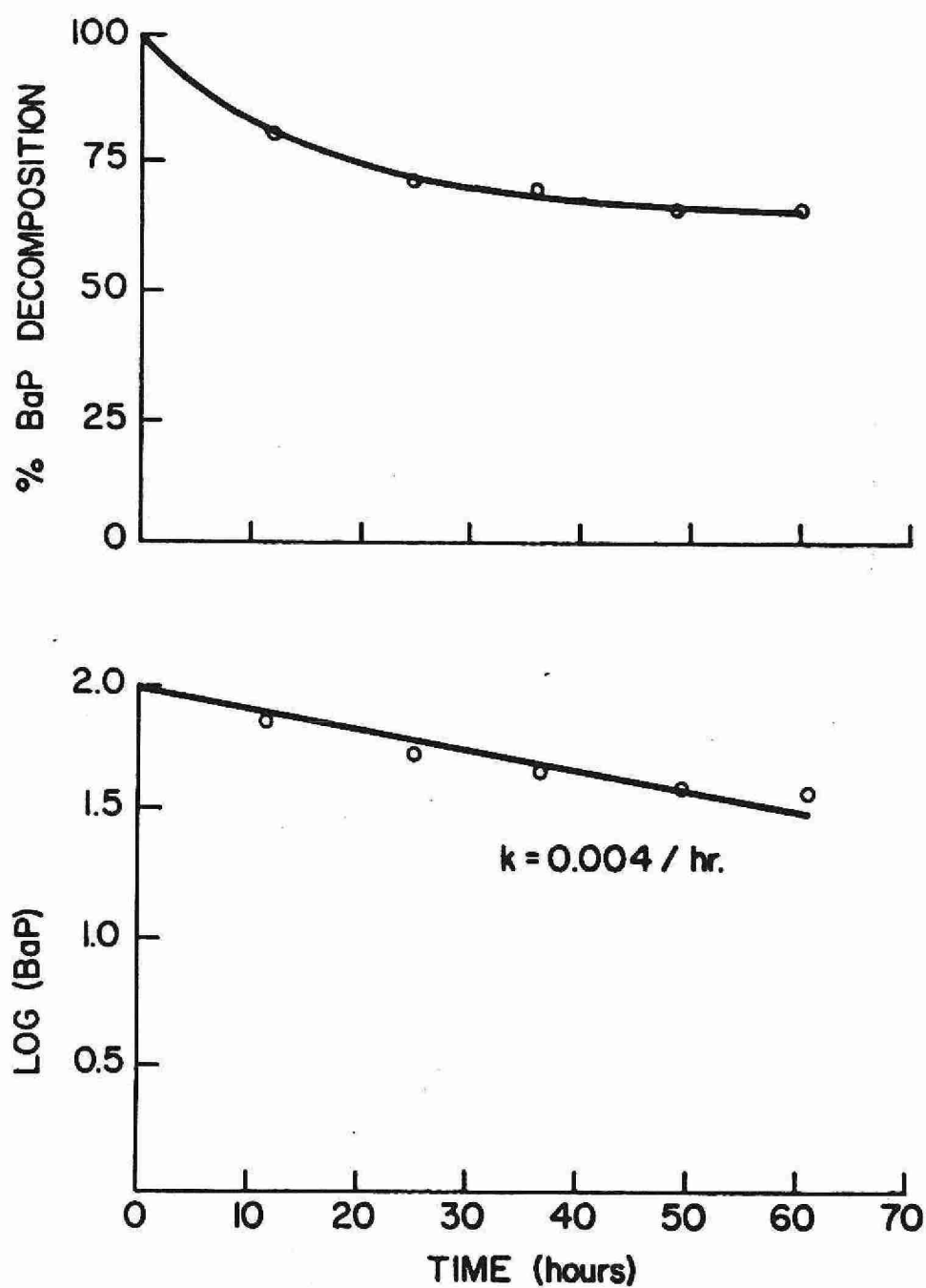


FIGURE 9. Photodecomposition of BaP in pond water ($\lambda = 300$ to 400 nm)

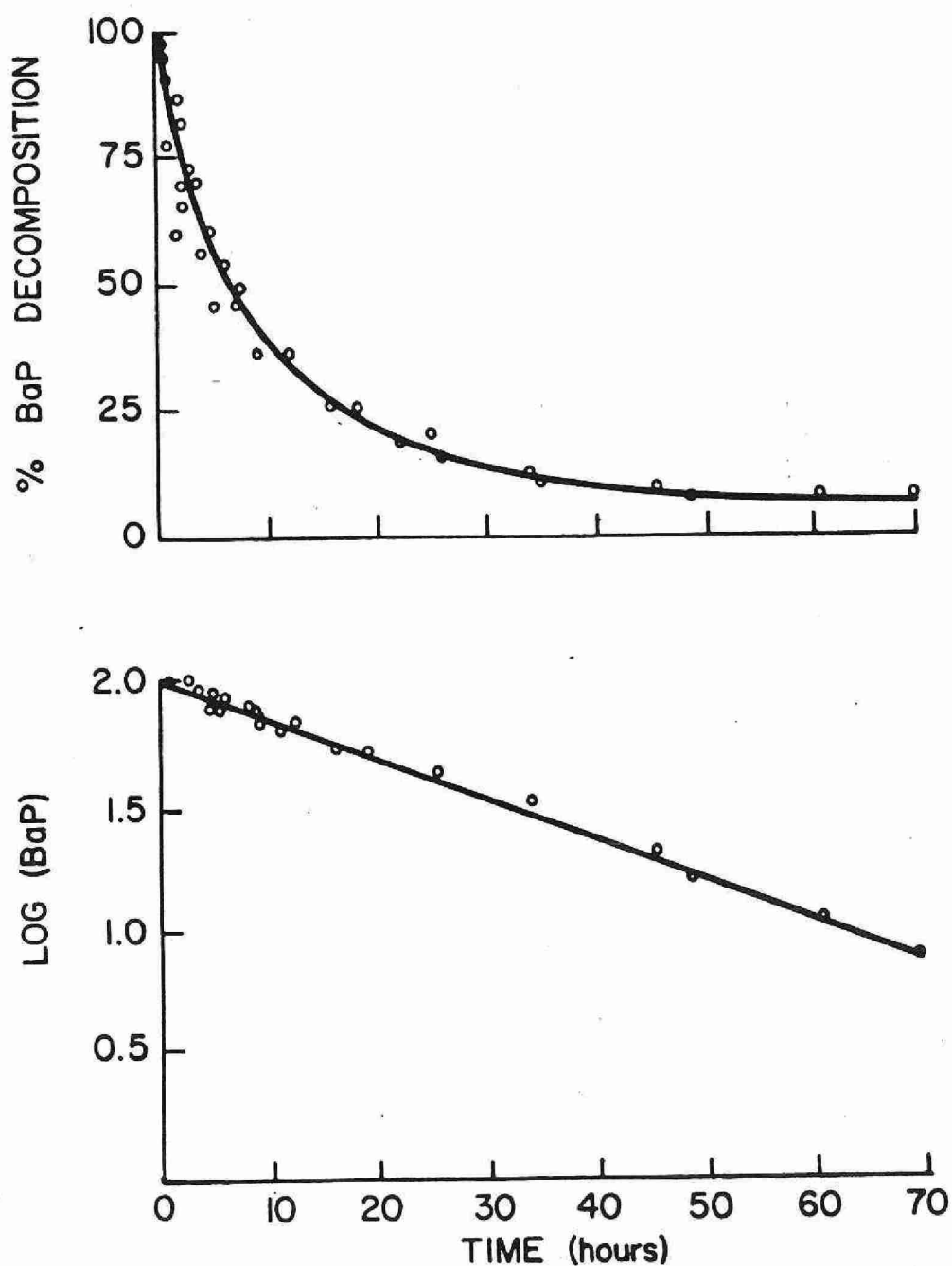


FIGURE 10. Photodecomposition of BaP in pond water with added fulvic acid ($\lambda = 300$ to 400 nm)

solutions with added fulvic acid, in the absence of oxygen.

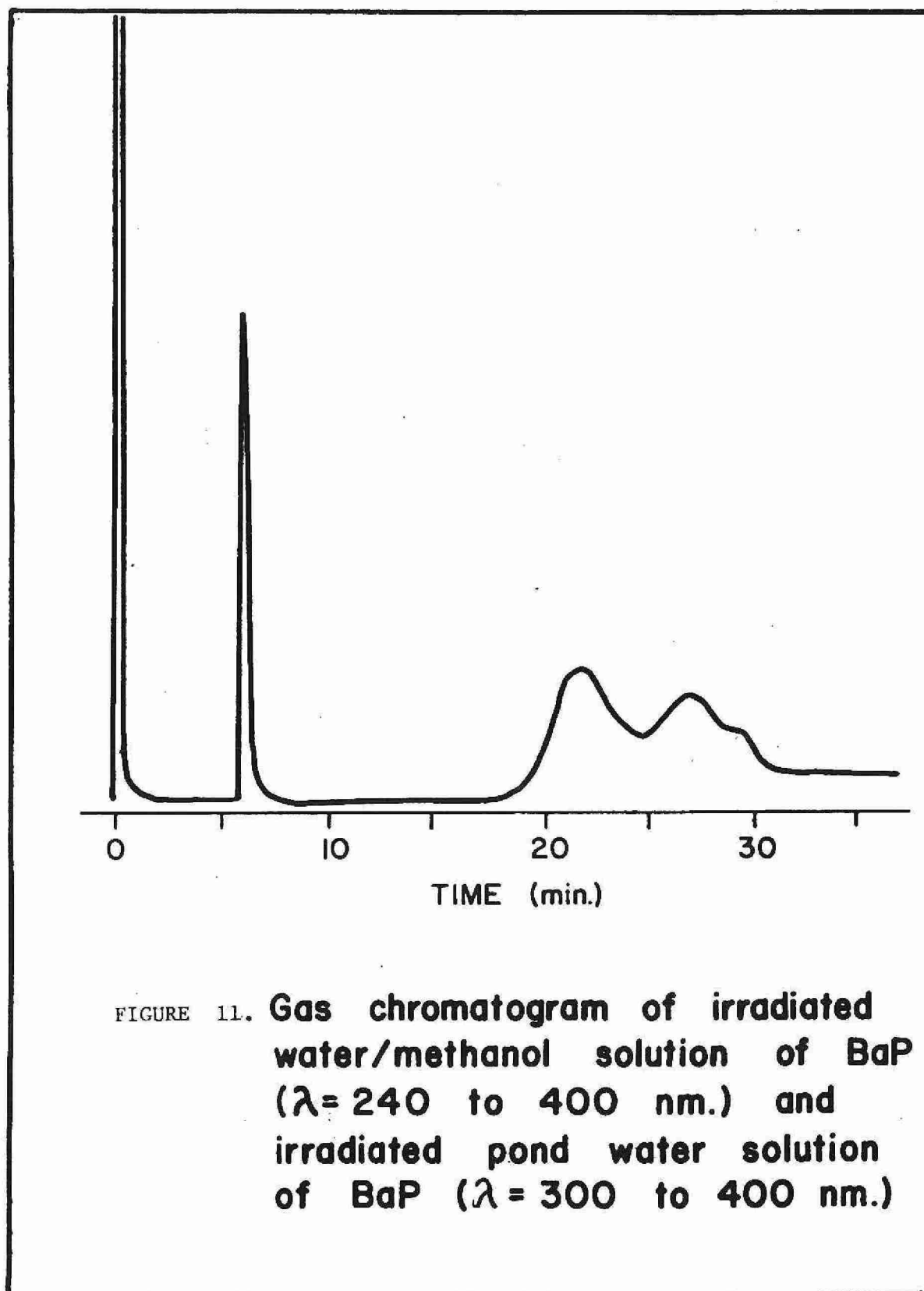
5.3 IDENTITY OF PHOTOPRODUCTS

After six hours of irradiation of methanol/water solutions of BaP (under wavelengths of 240 to 400 nm), of pond water solutions of BaP (under wavelengths of 300 to 400 nm) and of pond water solutions of BaP containing excess fulvic acid (under wavelengths 300 to 400 nm), a colour change in the solutions was observed. Particularly notable was the colour change in the concentrated chloroform extracts of the BaP solutions, which changed from yellow to dark orange after irradiation.

In addition to the colour change, there were changes in the gas chromatograms. For samples irradiated up to six hours, a steady decrease in the BaP concentration was observed by gas chromatogram and following BaP elution a group of three peaks appeared (Figure 11).

These peaks did not increase with additional irradiation of samples but stayed at a fairly constant height ($\pm 25\%$) up to 10 hours of irradiation. After this time they decreased to a low concentration, approximately equal to the detection limit.

Despite decreasing the temperature programming rate or decreasing the carrier gas flow, a baseline separation of the three peaks could not be achieved. However, it was possible to identify the three peaks as 1,6-, 3,6-, and 6,12-benzo(a)pyrene quinones on comparison of their retention times to a standard quinone solution.



To attempt a separation of the three BaP diones, it was decided to use a longer column. A capillary column had to be developed which was polar enough to separate the three BaP diones as well as being slightly apolar to elute BaP without excessive tailing.

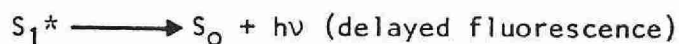
5.4 MECHANISM OF BaP PHOTODECOMPOSITION IN DEIONIZED WATER/METHANOL

It can be seen from the UV absorption spectrum of BaP that BaP absorbs strongly at wavelengths of 250 to 290 nm ($\log \epsilon = 4.8$) and of 360 to 390 nm ($\log \epsilon = 4.2$). A discussion of the formation and fate of the BaP excited states in these two regions will aid in the understanding of the photodecomposition of BaP.

Absorption by BaP of energy in the longer wavelength region ($\lambda = 360$ to 390 nm) excites BaP to its lowest excited singlet state (S_1^*). BaP (S_1^*) may undergo three transitions: (a) it may relax to the ground state (S_0) by emitting a quantum of light (fluorescence) or (b) it may lose energy as heat by relaxing to the S_0 state, or (c) it may undergo a radiationless transition to the first excited triplet state (T_1^*). This violates the spin conversion rule, but is a common occurrence (16) known as intersystem crossing (ISC).

The first excited BaP triplet state (T_1^*) has five possibilities whereby it can lose energy: (i) it can relax to the ground state (S_0) by emitting a quantum of light (phosphorescence), or (ii) BaP (T_1^*) can back intersystem cross (BISC) to S_1^* which will subsequently fluoresce to the ground state (S_0), or (iii) BaP (T_1^*) can react with a similar excited triplet state to produce a ground state BaP molecule and an

excited BaP molecule ($\text{BaP}(S_1^*)$). The excited BaP singlet will then fluoresce to the ground state (delayed fluorescence):



or (iv) T_1^* can chemically react with a second molecule which is also present in the triplet state, for example $O_2(^3\Sigma_g^-)$ present as a triplet in its ground state, or (v) a collision may occur between the excited triplet (T_1^*) and a ground state molecule to form an excited dimeric state.

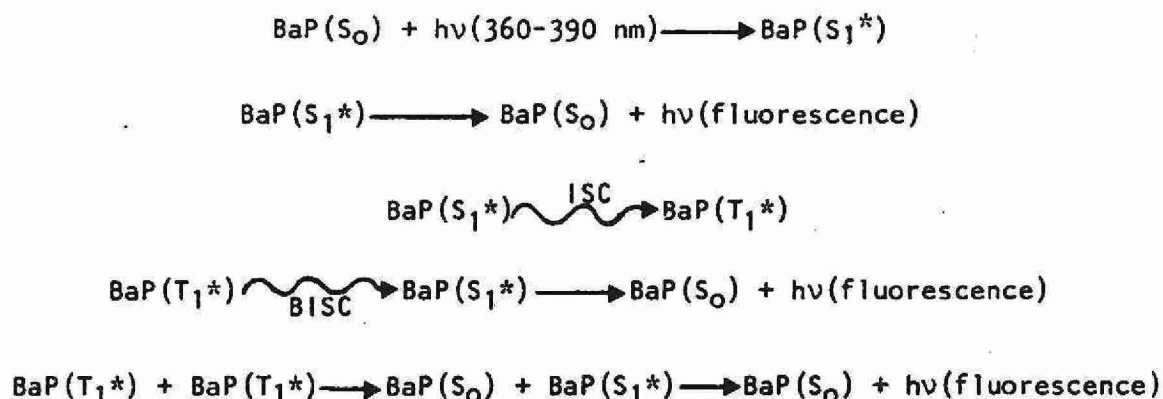
It has been shown (17) through experiments conducted on pyrene that a marked change occurs in the emission spectrum of pyrene upon an increase in concentration, from 10^{-4} M to 10^{-2} M. This behaviour was due to the formation of the excited dimeric pyrene at high concentrations. The BaP concentration in water/methanol is approximately 10^{-5} M, therefore the possibility of formation of an excited dimeric BaP molecule is low.

When BaP was excited by light of wavelength 368 nm, emissions were observed at 406 and 430 nm. No other broad emission bands at longer wavelengths characteristic of phosphorescence were seen. It is known (16) that significant phosphorescence does not normally occur at room temperature, in fluids.

It was also observed that fluorescence emissions at 406 and 430 nm were not quenched by oxygen implying that the first excited

triplet state does not react with ground state oxygen $O_2(^3\Sigma_g^-)$ to produce singlet oxygen. This phenomena would also account for the absence of oxygenated photoproducts as it is known PAHs react with singlet oxygen $O_2(^1\Delta_g)$.

Therefore, absorption of light by BaP in the region 300 to 400 nm will result in the formation of an excited first singlet state (S_1^*) which will subsequently undergo all fates leading to fluorescence or delayed fluorescence summarized as follows:



Absorption of light in the wavelength region of 250 to 290 nm by BaP in water/methanol will excite BaP to the second excited singlet state, S_2^* . $\text{BaP}(S_2^*)$ has two possible pathways, the first of which is radiationless deactivation to $\text{BaP}(S_1^*)$. The fate of $\text{BaP}(S_1^*)$ has been previously described for the longer wavelength region (360 to 390 nm): (a) fluorescence to S_0 or (b) radiationless deactivation to S_0 through heat release or (c) intersystem crossing to the T_1^* state. Radiationless transfer to the first excited triplet state, $\text{BaP}(T_1^*)$ was previously shown to result in back intersystem crossing to S_1^* , and subsequent

fluorescence but not formation of oxygenated photoproducts.

The second pathway of BaP(S_2^*) involves a radiationless transfer to the second excited triplet state (T_2^*). BaP(T_2^*) can either (a) react with another molecule in the triplet state, $O_2(^3\Sigma_g^-)$ or (b) react with a ground state BaP molecule to form an excimer or (c) radiationlessly deactivate to BaP(T_1^*).

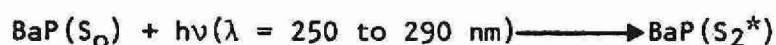
The possibility of BaP dimer formation at low concentrations (10^{-5} M) were previously dismissed by reference to pyrene dimer formation only at concentrations greater than 10^{-2} M.

From irradiations of air saturated BaP/water/methanol solutions at 240 to 400 nm, three BaP quinones were produced; whereas under nitrogen, no reaction occurred. It was also observed that emissions at 406 and 430 nm, produced from excitation at 254 nm, were 90% quenched by oxygen. Therefore, it can be concluded that the second excited triplet state reacts with ground state oxygen ($^3\Sigma_g^-$) and probably leads to formation of singlet oxygen, $O_2(^1\Delta_g)$. It can also be concluded that the low percentage (approx. 10%) of T_2^* which does not react with oxygen will follow the pathways which lead to fluorescence or delayed fluorescence.

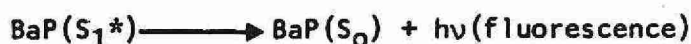
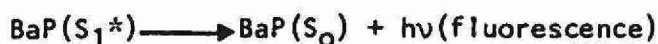
To further prove the presence of $O_2(^1\Delta_g^-)$ as the reactive intermediate in the oxygenations of BaP to form BaP-quinones, the following simple experiment was conducted.

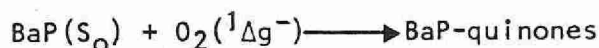
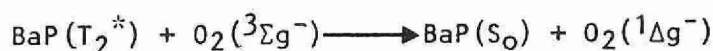
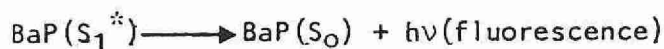
Rose Bengal, a known singlet oxygen sensitizer (18,19) was

irradiated in a BaP/water/methanol solution. The same three quinones that had been identified as photoproducts from irradiation of BaP at 240 to 400 nm in water/methanol were found as photoproducts of Rose Bengal sensitized photooxygenation of BaP. Therefore, the presence of singlet oxygen as the reactive intermediate in photooxygenations of BaP in the 240 to 400 nm wavelength region was confirmed. Thus the primary mechanism that occurs upon irradiation of BaP under wavelengths of 240 to 400 nm is:



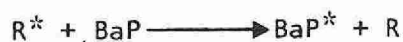
Since some fluorescence under an air atmosphere does occur, the pathways leading to fluorescence must be included. Therefore the entire mechanism is as follows:





5.5 MECHANISM OF BENZO(a)PYRENE PHOTODECOMPOSITION IN POND WATER

Irradiations of BaP dissolved in pond water, under light of wavelengths 300 to 400 nm resulted in decomposition of BaP, to form three BaP diones. It was shown previously that BaP does not react in deionized water under these wavelengths, 300 to 400 nm, therefore, in pond water there may be an energy transfer occurring from a dissolved species to BaP. This energy transfer is referred to as "sensitization" and is illustrated by the general reaction:

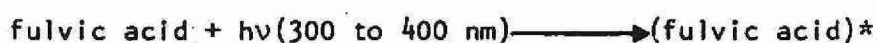


where R and R^* is a dissolved organic in the ground state respectively.

Energy transfer from R^* to BaP in this sensitized reaction will produce only the $\text{BaP}(T_1^*)$ state, which has been previously shown not to photoreact. Therefore, another type of mechanism must be important in

pond water to induce a BaP photodegradation in the wavelength region 300 to 400 nm.

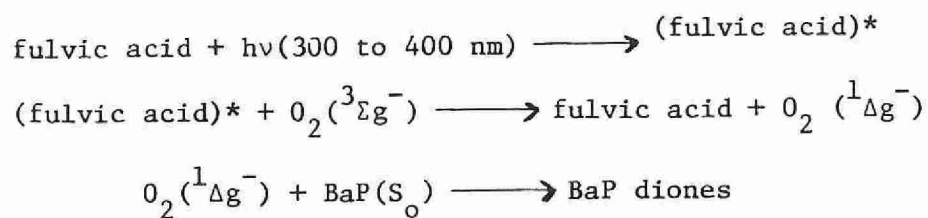
Zepp et al (20) have recently observed that photooxygenations of various PAHs does occur in water containing high concentrations of dissolved organics. They hypothesized that the sensitizer under these conditions was fulvic acid but that the reactive intermediate was singlet oxygen:



It was shown experimentally that the BaP decomposition rate in pond water ($\lambda = 300$ to 400 nm) increased over that in deionized water ($\lambda = 240$ to 400 nm). Also, it was apparent that the rate of decomposition of BaP in pond water was directly proportional to the concentration of fulvic acid in the water, and that the rate was quenched entirely in the absence of oxygen.

The photoproducts from fulvic acid sensitized decomposition of BaP ($\lambda = 300$ to 400 nm) were identical to those found from Rose Bengal sensitized photooxygenations. It was known that the reactive intermediate in the Rose Bengal photooxygenations was singlet oxygen, therefore, it can be concluded that irradiation of fulvic acid under wavelengths found in sunlight, 300 to 400 nm, does produce singlet oxygen, $\text{O}_2(^1\Delta_g^-)$. Thus, it can be concluded that, in pond water, for the photooxygenation of BaP under light of wavelengths 300 to 400 nm, the mechanism can be

represented as follows:



The detection of the photooxygenated products, 1,6-, 3,6- and 6,12-benzo(a)pyrene diones, from irradiations of BaP in natural water, becomes very significant when the carcinogenicity of such compounds is considered. Various researchers (21,22,23) have found that oxygenated BaP derivatives such as the 1,6-, 3,6- and 6,12-BaP quinones, induce sarcomas in test animals. It may yet be proven that these derivatives of benzo(a)pyrene become ultimate carcinogens to man.

Additional information on the photodecomposition of BaP in aqueous media may be obtained by reference to the Thesis of Helle M. Tosine (24).

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